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# Summary of Gas Stream Control Technology for Major Pollutants in Raw Industrial Fuel Gas

**Hydrocarbon Research, Inc, Lawrenceville, NJ**

Prepared for

**Industrial Environmental Research Lab, Research Triangle Park, NC**

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Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

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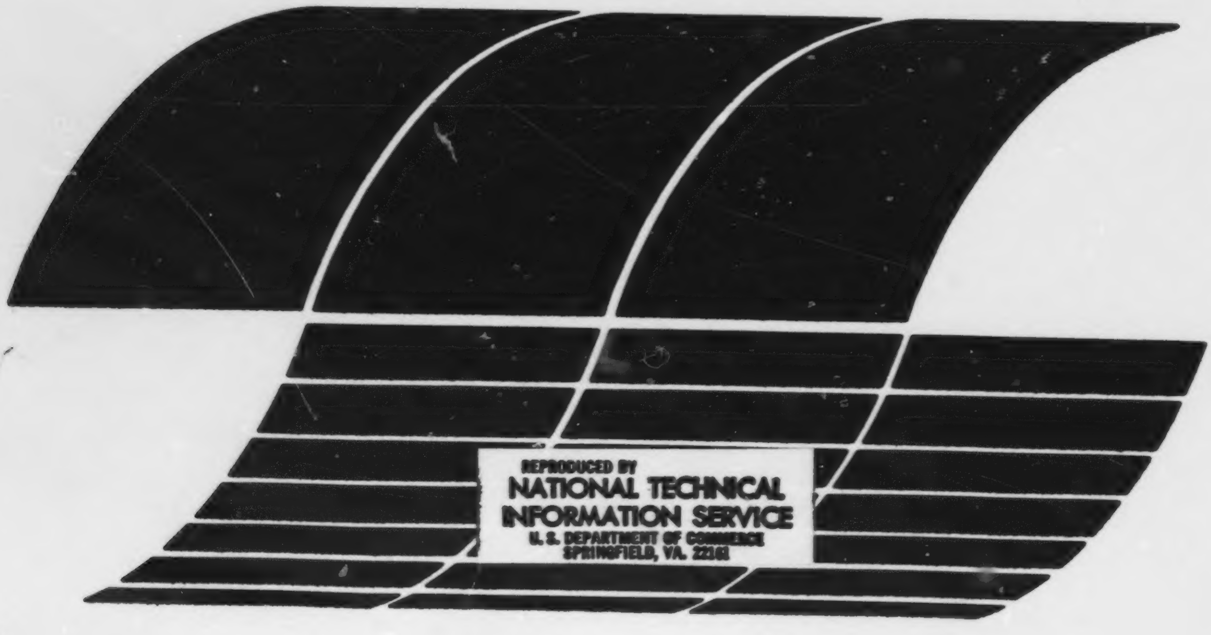
## Interagency Energy/Environment R&D Program Report



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16. ABSTRACT

The report summarizes coal gasification and clean-up technology with emphasis on methods of producing a clean industrial fuel gas as defined by agreement for study purposes. The coal-derived industrial fuel discussed produces no more than 0.5 lb of $SO_2$, 0.4 lb of $NO_x$, and 0.1 lb of particulates per million Btu of fuel gas. In general, existing state-of-the-art control technology will allow these emission guidelines to be met, although the end use for the fuel gas will strongly influence the choice of the pollution control technology that is used. Many but not all important factors pertinent to control technology application were considered. Costs are an example of important factors which were not evaluated because the objective was to first determine appropriate technology that could be applied. Emissions other than the three major pollutants indicated were given only cursory treatment. Nevertheless, a general overall background of control technology for industrial fuel gas has been covered.

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| Goal Gasification | Dust | Stationary Sources | 13H | 11G |
| Coal | | Industrial Fuel Gas | 21D | |
| Gases | | Particulate | 07D | |
| Fuels | | | | |
| Sulfur Dioxide | | | 07B | |

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# Summary of Gas Stream Control Technology for Major Pollutants in Raw Industrial Fuel Gas

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Prepared for

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## ABSTRACT

This report is a summary of coal gasification and clean-up technology with emphasis on methods for producing a clean industrial fuel gas as defined by agreement for study purposes. The coal-derived industrial fuel discussed is one which produces no more than 0.5 lbs of $SO_2$, 0.4 lbs of $NO_x$ and 0.1 lbs of particulates per million Btu of fuel gas. In general, existing state-of-the-art control technology will allow these emission guidelines to be met although the end use for the fuel gas will strongly influence the choice of the pollution control technology that is used.

Many but not all important factors pertinent to control technology application were considered. Costs are an example of an important factor which was not evaluated because the objective was to first determine appropriate technology that could be applied. Emissions other than the three major pollutants indicated were given only a cursory treatment. Nevertheless, a general overall background of control technology for industrial fuel gas has been covered.

## SUMMARY

Industrial fuel gas, classified as a fuel whose combustion products exhaust directly to the atmosphere, logically fits into emission guideline levels established by the Clean Air Act of 1971 even though the $SO_2$ emission level was not specifically covered by that regulation. For this reason, tentative guidelines for emissions of 0.5 lbs $SO_2$, 0.4 lbs $NO_x$ and 0.1 lbs of particulates per million Btu of coal-derived gaseous fuel were selected for study purposes. With worsening fuel shortages, the importance of industrial fuel gas is expected to increase and its manufacture and control technology should be examined.

Commercially available gasification and clean-up technology, as individually described, has promised, even if not yet demonstrated, the availability of systems to convert coal into fuel gas while controlling at least sulfur, nitrogen and particulates to levels satisfactory for pipeline gas. The less stringent standards for industrial gas, as illustrated by the lower percent removal of major pollutants, are then within reach with some imaginative design because new or previously rejected technology might be appropriate under such circumstances. Since this lowered clean-up requirement makes it possible to reconsider some old technology as well as modern processes, design techniques and typical design for the use of iron-oxide processes have been made and compared to the Stretford process.

End use of the fuel gas must also be considered. If the fuel is used in a cement kiln, clean-up requirements might be minimal because $SO_2$ would be removed in the cement-making process and particulate control of process exhaust gas would preclude the need for

particulate removal from fuel gas. Carbon dioxide, which need not be removed from industrial fuel, may lessen thermal $NO_x$ formation due to cooler combustion.

While sulfur removal is covered in some detail, the problems of nitrogen, tar and particulates also are considered. High levels of nitrogen compounds may deactivate or cause losses in the sulfur clean-up processes. Consequently, when nitrogen levels are high, HCN might be controlled by an HCN guard or polysulfide scrubbing and basic nitrogen compounds with acid scrubbing. Use or disposal of tars require more study because of the high sulfur and nitrogen contents. Combustion of a typical tar from coal gasification would probably yield a flue gas exceeding $NO_x$ emission guidelines. By-product tar utilization is, therefore, a fertile field for future research. Particulate control technology demonstrates capability to achieve at least 0.0001 grains per SCF while the industrial fuel guideline has been estimated to be 0.1 grains per SCF. Technology is available and the proper control systems can then be selected to meet the particulate level required for specific industrial fuel use.

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## INTRODUCTION

Gas manufactured from coal (General Reference #6) was first produced in the late 18th century by heating coal in the absence of air. To supply the necessary heat, additional coal was burned outside of the vessel. Combustion gases were segregated from the air-deficient interior gas. By 1812, the first coal-gas company was chartered in London to distribute a product used for lighting. Four years later, the first U.S. company was chartered in Baltimore.

Initially, gas with a heating value ranging from 475 to 560 Btu per cubic foot (depending on the type of coal and process conditions) was produced by destructive distillation of coal. Coke ovens, which manufacture coke mainly for steel industry use, produce an off-gas similar in composition. This coke-oven gas, where available, often supplemented the supply of coal gas made from plants involving the destructive distillation of coal. Unfortunately, about 70 percent of the feed coal remains as a solid residue in these processes and disposal of the residue was a problem except in the coking-type operation where coke was the primary product. The solution to the disposal problem for the carbon-rich residue lead a step beyond distillation to gasification of the residue.

Coal gasification, which depending on the process may in the same vessel be preceded by distillation, involves the subsequent reaction of the solid with air or oxygen and steam. The distillation step gases which are first released have a high Btu content because methane and higher hydrocarbons contained in the coal are among the first components to emerge as the coal decomposes. The gasification step makes a gas with a much lower heating value because the gas produced is essentially a mixture of carbon monoxide, carbon dioxide and hydrogen.

The gasification of coal follows two basic paths, using either air or oxygen supported combustion to supply required heat. This heat-producing step is necessary to maintain endothermic gasification reactions. Gasification with air produces a clean gas of low (100-250 Btu/cu.ft.) heating value due to a significant concentration of nitrogen introduced in the air supply. To make a low inert content gas suitable for synthesis, it is necessary to gasify with oxygen. This second route produces clean gas of either medium (250-550 Btu/cu.ft.) or high (950-1000 Btu/cu.ft.) heating value. The latter case requires additional process steps to reach the higher heat content and, as such, is not pertinent to the basic objective of this overview which is limited to the study of industrial fuel.

Industrial gaseous fuels can generally be classified as low or medium Btu fuels that are burned in equipment designed to exhaust the products of combustion through a chimney directly to the atmosphere. On the other hand, pipeline or "towns-gas" quite often discharge the products of combustion directly into a closed environment such as a house or factory. In such an environment, the combustion products are comingled with air and can be breathed by humans. For example, the typical household gas stove or oven is often poorly vented or not vented at all. Hence, the products of combustion from the gaseous fuel are breathed in a diluted form in the home. Consequently, the sulfur content of pipeline gas is severly restricted to accommodate this probability, and the maximum sulfur level permitted in pipeline gas is about 4 ppm (1/4 grain per 100 SCF).

Conversely, industrial fuel gases used to fire kilns, boilers, heat-treating furnaces, etc., are combusted in equipment fitted with appropriate stacks for discharge of the products of combustion directly to the atmosphere. Therefore, it follows that the pollution effects of the fuel-gas can be assessed on a more global basis, using criteria more related to ambient concentrations of pollutants that can be expected at ground levels.

These assessments already have been made and the Clean Air Act of 1971 specifies that the large-scale burning of fuels conform to these New Performance Standards for units that started construction after August 17, 1971.

### BOILER EMISSIONS STANDARDS
### (HEAT INPUT GREATER THAN $250 \times 10^6$ BTU)

Reference: W.C. Wolfe, "Controlling Industrial Boiler Emissions", PLANT ENGINEERING, 1/24/74

| Emission | Fuel | lb/$10^6$ Btu Input | Approx. ppm (dry) |
|---|---|---|---|
| Particulate | All | 0.1 | (0.12 grains per SCF) |
| $SO_2$ | Liquid | 0.8 | 550 |
| | Solid | 1.2 | 520 |
| $NO_x$ | Gaseous | 0.2 | 165 |
| | Liquid | 0.3 | 227 |
| | Solid | 0.7 | 525 |

However, the Clean Air Act failed to specify the allowable emissions of $SO_2$ when burning gaseous fuels, presumably because the gaseous fuels then currently burned were of pipeline quality and the resultant fuel-gases were innocuous. The absence of a sulfur specification for gaseous fuels should not be interpreted as requiring zero pollutant emissions from such fuels. A rational analysis of the fuel substitution problem would suggest that permissable sulfur levels in gaseous industrial fuels should be close to, but less than, levels for liquid and solid fuels. Lower sulfur levels in the gas might be implied by analogy to the $NO_x$ level for a gas as compared to liquid and solid fuels.

It is, therefore, possible to infer permissable emissions levels that would conform in principle with the Clean Air Act criteria. For the purpose of conducting the study from which the summary of control technology would be developed and to determine if control technology required would be significantly reduced from that necessary for pipeline gas, discussions with the Fuels Process Branch of the EPA led to the following guideline pollutant levels for coal-derived industrial fuel gas. Although these emission specifications provide a basis for study, no regulation by the EPA is implied or recommended by their use.

| Pollutant | Maximum Emission Level |
|---|---|
| Sulfur | 0.5 lbs $SO_2$ per $10^6$ Btu |
| Nitrogen | 0.4 lbs $NO_x$ per $10^6$ Btu (measured as $NO_2$) |
| Particulates | 0.1 lbs per $10^6$ Btu |

Note that the suggested nitrogen level is twice the nitrogen level in the 1971 Clean Air Act. This increase in the allowable nitrogen level for industrial fuel gas recognizes the fact that coal-derived fuel gases may contain nitrogen compounds not normally found in natural gas. As a consequence, the $NO_x$ that is formed during combustion is derived from fuel-bound nitrogen and also from the thermal fixation of atmospheric nitrogen itself. Thus, the anticipated $NO_x$ levels when burning coal-derived industrial fuel gas are higher than the levels expected when combusting natural gas (which has no fuel-bound nitrogen).

Therefore, it can be said that industrial gas is a fuel that can be expected to produce more pollutants than natural (pipeline) gas when burned but less pollutants than liquid or solid fuels. As the natural gas shortage worsens, the use of industrial gas to replace natural gas can be anticipated especially in instances where liquid or solid fuels are difficult or impossible to burn as substitutes.

Suitable control technology for fuel converters producing industrial fuel gases must be developed in order to assure an acceptable environment. This is not to say that acceptable control technology is not available, but just that previous applications either lacked control or applied them to more stringent standards such as synthesis gas. A review of existing gasification processes that have had a history of successful commercial operation suggests that operable systems have already been developed to reduce and control the particulate, sulfur and nitrogen content of coal-derived fuel gases to meet process requirements. Since these process requirements are more stringent than the emission levels discussed previously for industrial fuels, the control technology that they use should be satisfactory with a little adaptation to the guideline levels. The purpose, then, of this overview is to discuss operable gasification systems to cover clean-up methodology, and to suggest improved methods for raw gas clean-up that will result in an industrial fuel gas that meets the proposed guidelines.

A review of many coal gasification systems that are capable of producing an industrial fuel gas from coal is presented in the following section of the report. Only those systems which have some degree of proven operability have been considered. Economics were not considered in choosing which processes should be included in this review.

Processes selected for review are as listed below:

- Koppers-Totzek
- Lurgi
- Riley-Morgan
- Wellman-Galusha
- Wilputte
- Winkler
- Woodall-Duckham/Gas Integrale

Air-blown as well as oxygen-blown data are included where available.

## CONCLUSIONS AND RECOMMENDATIONS

o The purpose of this overview was to assess the capability for producing an industrial fuel gas that will meet the following environmental guidelines:

Maximum 0.5 lb $SO_2$/MM Btu fuel gas
Maximum 0.4 lb $NO_x$/MM Btu fuel gas
Maximum 0.1 lb particulates/MM Btu fuel gas

Technologies exist today that can meet these standards. However, the best choice of pollutant control systems is dependent upon the type of coal gasifier, the coal utilized and the end use of the fuel gas.

- Industrial fuel gas standards are less stringent than those required to produce a pipeline gas and this allows a wider choice of systems.

- The utilization of tars produced, the disposal of spent liquors from acid gas removal, and the clean-up of waste water must be considered when developing the appropriate processing sequence for manufacture of environmentally acceptable industrial fuel gas.

- Coals containing high nitrogen and sulfur will produce tars which are too high in nitrogen and sulfur to permit the tars to be burned directly as fuel and still meet the standards set by the Clean Air Act of 1971 for liquid fuels. A fertile field for future development is to establish economic methods for removal of sulfur and nitrogen from tar.

- Only recently has much consideration been given to environmentally acceptable methods for disposal of spent acid gas removal liquors. This is an area which requires additional development.

- A significant cost in producing an acceptable industrial fuel is the clean-up of the waste water leaving the particulates removal system. Therefore, it is important to use methods for particulates removal which minimize the quantity of waste water.

## SECTION A - DESCRIPTION OF GASIFICATION SYSTEMS

1. **Discussion of Basic Technology**
2. **Koppers-Totzek**
3. **Lurgi**
4. **Riley-Morgan**
5. **Wellman-Galusha**
6. **Wilputte**
7. **Winkler**
8. **Woodall-Duckham/Gas Integrale**

## A.1 Discussion of Basic Technology

Means for the production of gaseous products from coal have been known for many years, and commercial processes for coal gasification are available. Currently, considerable effort is being expended to develop efficient means for producing gaseous products from coal suitable for use as an energy source that meets environmental regulations.

Gasification of coal transforms a cumbersome, inconvenient, dirty solid fuel into a convenient, clean, gaseous fuel or into synthetic gas. Some of the heating value of the coal is expended to accomplish this transformation.

Primary gasification of coal entails the treatment of coal with air or oxygen and steam to yield a combustible gaseous product. The product of primary gasification obtained from devolatilization of coal and reaction of coal carbon with the gasifying agent is usually a mixture of $H_2$, CO, $CO_2$, $CH_4$, inerts (such as $N_2$), and minor amounts of higher hydrocarbons (such as tar, $C_2H_6$, $C_2H_4$, etc.) and impurities (for example, $H_2S$, $NH_3$ and dust). The product gas is called a low Btu gas if an air-steam mixture is used directly to gasify the coal and it contains nitrogen as a major component. Low Btu gas is suitable for use as an energy source near its point of generation. Intermediate Btu gas (synthesis gas), which contains only a small amount of nitrogen, is obtained when an oxygen-steam mixture is used to gasify the coal. Intermediate Btu gas can be used either as an energy source or as a synthesis gas for the production of chemicals and synthetic liquid and gaseous fuels.

Three basic reactor concepts have been developed for the gasification of coal. These are:

1. Fixed-bed or moving-bed (i.e., Lurgi reactor).
2. Fluidized-bed (i.e., Winkler reactor).
3. Suspension or entrained reactors (i.e., Koppers-Totzek).

In a moving-bed reactor, the gasifying medium is passed countercurrent to the coal with ash removal from the bottom and coal addition at the top. If the velocity of the gasifying medium and the size of the coal particles are such that the bed behaves as a fluid, the system is called a fluidized bed. An entrained system operates with pulverized coal particles carried by the gasifying medium.

Generally, a gasification reactor can be divided into three zones: the devolatization, gasification and combustion zones. In the devolitization zone, if the gasifier has one, coal is dried and carbonized by hot gas. Most of the volatile matter and moisture of coal is distilled as $CH_4$, tar and aqueous compounds. In the gasification zone, carbon in the coal reacts with steam and carbon dioxide to produce carbon monoxide and hydrogen. Both the devolatization and gasification zones are endothermic. The third zone is a combustion zone in which coal is oxidized to CO and $CO_2$. The heat generated in the combustion zone sustains the chemical reactions in the gasification and devolatization zones.

The principal components of the product gas are formed by a combination of the following reactions:

(A) Heat generation reactions

$$C + O_2 = CO_2 + \text{Heat}$$

$$C + 1/2\ O_2 = CO + \text{Heat}$$

(B) Heat consumption reactions

$$C + H_2O + \text{Heat} = CO + H_2$$

$$C + CO_2 + \text{Heat} = 2\ CO$$

The compositions of numerous producer gas products have been examined to gain a better understanding of the performance of gas generating systems. Data from various types of autothermic noncyclic gas generators have been plotted in Figures A-1.1 and A-1.2. Yield patterns on air-blown as well as oxygen-blown systems have been plotted. The bulk of the data is from coal-based gasifiers but some data is included from oil-based systems for comparison. As would be expected, the data from coal and oil-based units correlate separately because of different C/H ratios in the feed material. Figure A-1.1 is a plot of the yield of $CO + CO_2$ vs. $CO + H_2$. These data points follow a well-defined yield pattern and correlate well considering the variety of feed coals and the wide range of system pressures involved in the correlation. It should be emphasized that this correlation applies to noncyclic systems only. Cyclic systems, due to the separation of the blow gas from the run product gas, follow a different yield pattern. The ratio of $CO + CO_2$ to $CO + H_2$ indicates the extent of coal combustion versus gasification and is less than 1.0, as indicated by the slopes of the lines in

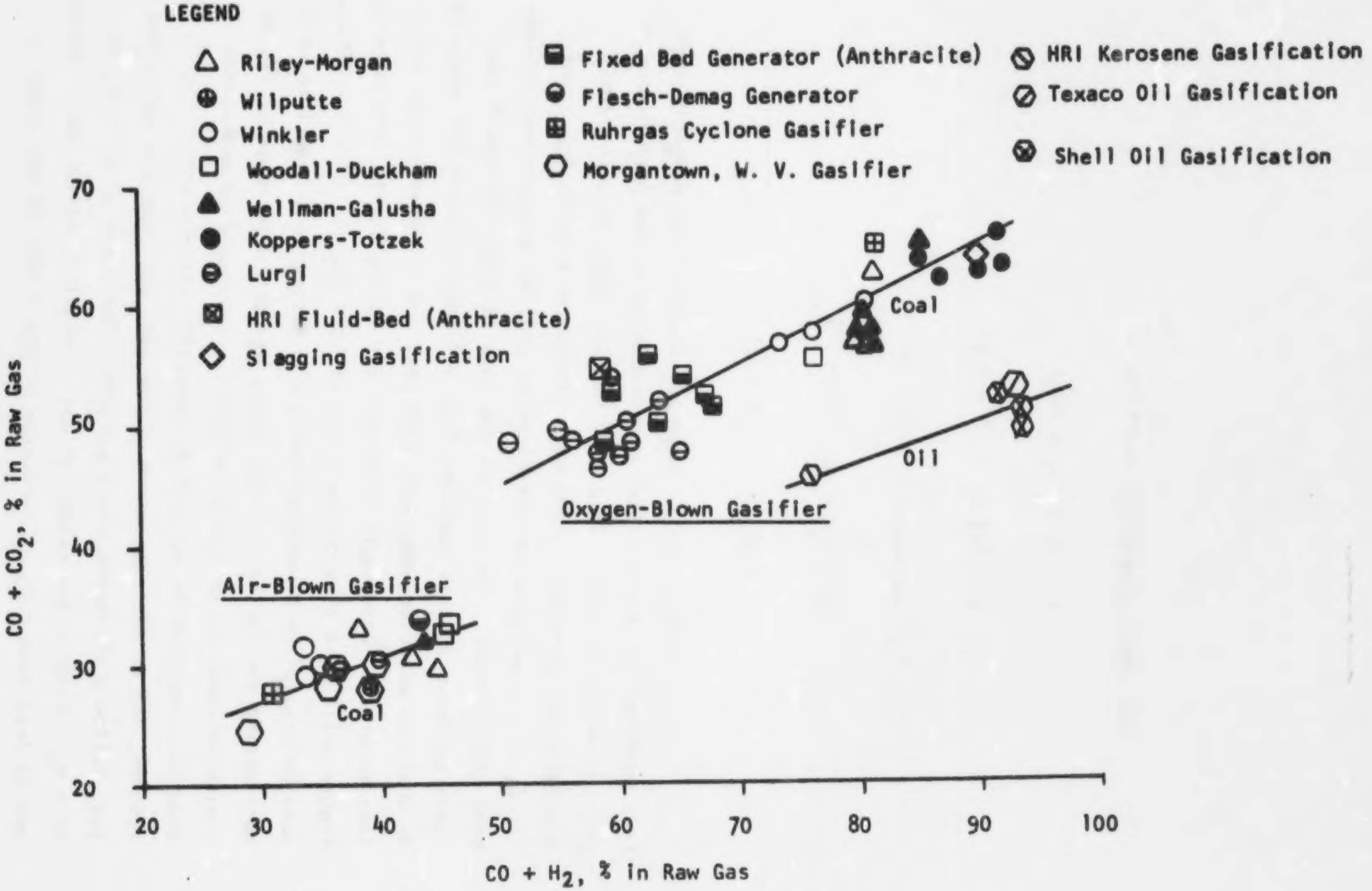
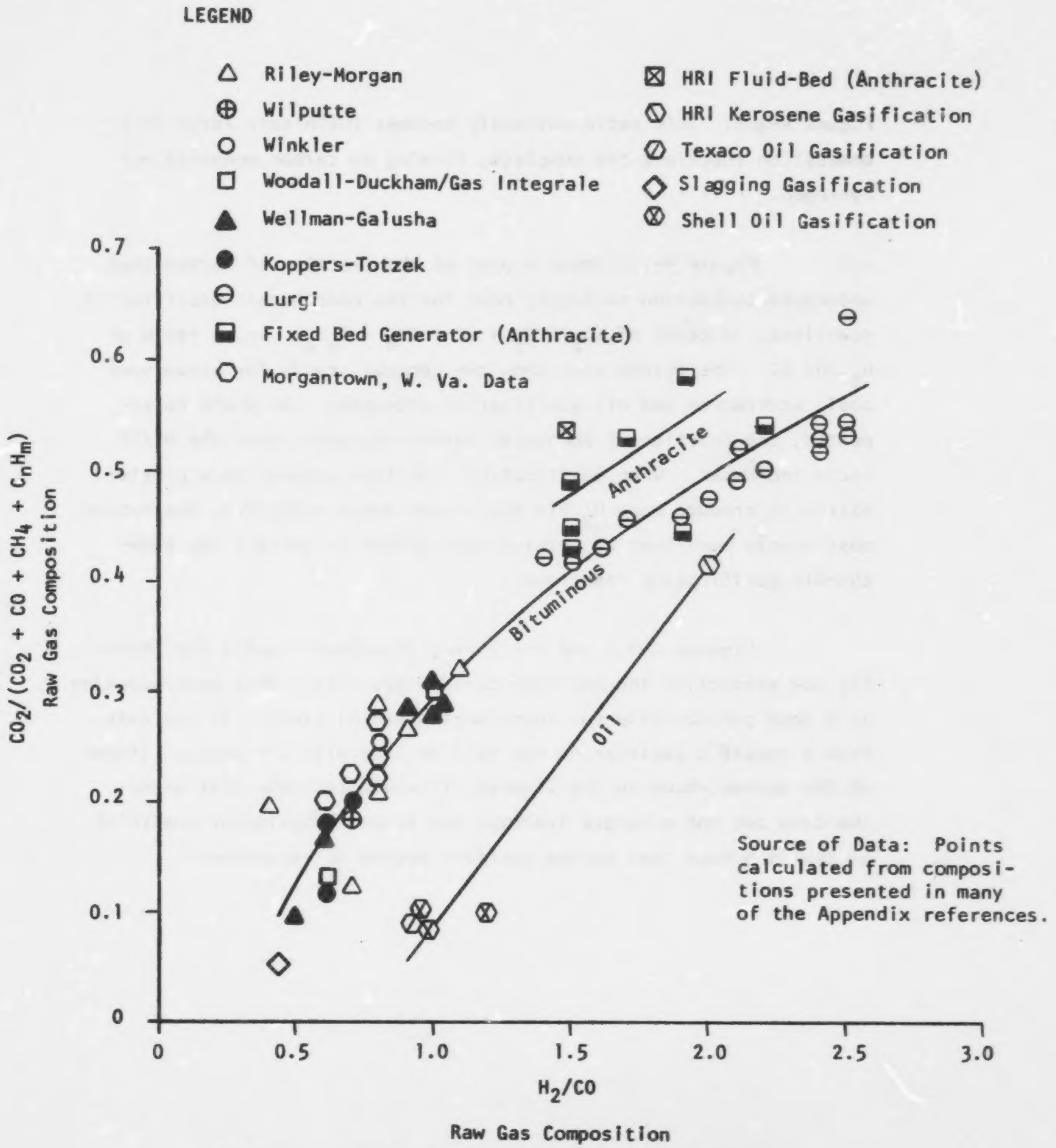


FIGURE A-1.1 GENERALIZED PERFORMANCE OF GASIFIERS

Source of Data: Points calculated from compositions presented in many of the Appendix references.



Source of Data: Points calculated from compositions presented in many of the Appendix references.

FIGURE A-I.2 GENERALIZED PERFORMANCE OF GASIFIERS

Figure A-1.1. This ratio obviously becomes infinitely large when combustion reactions are complete, forming no carbon monoxide and hydrogen.

Figure A-1.2 shows a plot of the fraction of carbon that undergoes combustion to supply heat for the endothermic gasification reactions, in terms of $CO_2/(CO_2 + CO + CH_4 + C_nH_m)$ vs. a ratio of $H_2$ and CO. The curves also show the general trends for bituminous coal, anthracite and oil gasification processes. As would be expected, the fraction of combusted carbon increases when the $H_2/CO$ ratio increases. When gasification reactions proceed to a greater extent to produce more $H_2$ via the steam-carbon reactions, the system must supply more heat by burning more carbon to sustain the endothermic gasification reactions.

Figures A-1.1 and A-1.2 are, therefore, useful for checking and predicting the performance of a gasifier. This understanding is a good prerequisite for sound environmental study. If the data from a specific gasifier do not fall in line with the general trends of the curves shown in the figures, it would indicate that either the data are not accurate (perhaps due to bad sampling or analysis) or that the heat leak on the gasifier system is excessive.

## A.2 Koppers-Totzek Process

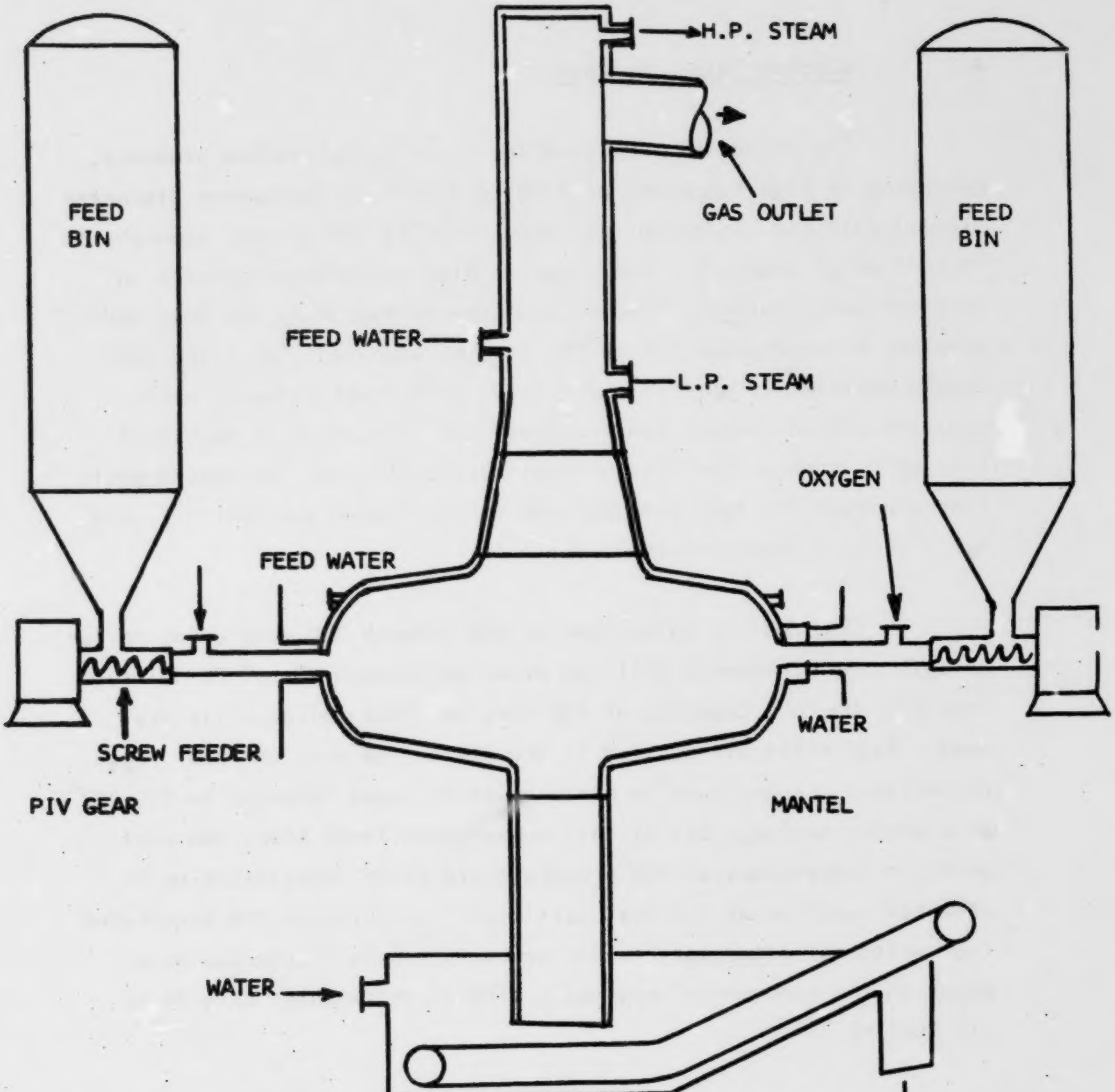
The Koppers-Totzek gasifier is an entrained-bed producer, operating at high temperature (3300 to 3500°F at the burner discharge with an exit gas temperature of about 2700°F) and at near atmospheric (5 to 7 psig) pressure. Operation at high temperature results in complete gasification of carbon and organic sulfur in the feed and produces a nonreactive ash in the form of a molten slag. The two-headed gasifier is a refractory-lined, horizontal cylinder with opposing coaxial burner heads at each end. Capacity of each gasifier unit is about 400 tons of coal per day for the two-headed gasifier and over 800 tons per day with a four-headed gasifier. Figure A-2.1 shows a Koppers-Totzek unit.

The coal is pulverized to 70% through 200 mesh using roller or ball type wind-swept mill and dried to between 2% and 8% moisture content. Up to a capacity of 150 tons per hour roller mills are used. Ball mills are applied in the 150 to 250 tons per hour range. Pulverizers are designed to use combustion gases tempered to 800-900°F as a drying medium. Gas at this temperature level keeps the coal particle temperature at 180°F where there is no devolitization or chemical reaction of the coal particles. As a result the evaporated coal moisture, after particulate removal, can be discharged as a vapor to the atmosphere reportedly without detrimental affects to air quality.

The dried, pulverized coal is conveyed with nitrogen to gasifier service bins and continuously discharged from twin variable-speed screw feeders into a mixing nozzle where it is entrained in a mixture of oxygen and low pressure steam. The feed mixture is then delivered through

FIGURE A-2.1

KOPPERS TOTZEK GASIFIER


H.P. STEAM
GAS OUTLET
FEED BIN
FEED BIN
FEED WATER
L.P. STEAM
OXYGEN
FEED WATER
WATER
SCREW FEEDER
PIV GEAR
MANTEL
WATER
ASH

Reference: Koppers Company Brochure

a transfer pipe to the burner head of the gasifier at a speed higher than flame velocity. Moderate temperature and high burner velocity prevent the reaction of the coal and oxygen until entry into the gasification zone. The gasifier designs either have two or four gasifier heads with opposed inlets. Alignment of in-flow lines is offset to create a cyclone for effective mixing. The steam shrouds the high temperature reaction zone and protects burners and refractories from excessive temperature in addition to its principal role of supporting the gasification reactions. Product gas passes through a central, water-cooled vertical gas outlet. Some ash (30% to 50%), in the form of a molten slag, leaves the gasifier with the product gas; the balance (50% to 70%) is removed from the bottom of the gasifier.

The raw gas from the gasifier passes through the waste heat boiler where high pressure steam (up to 1500 psig) is produced. After leaving the waste heat boiler, the gas at 350°F is cleaned and cooled in a high energy scrubbing system. Particulate-laden water from the gas cleaning and cooling system is piped to a clarifier. The cool gas leaving the gas cleaning system may contain sulfur compounds which must be removed to meet gas specifications.

A list of Koppers-Totzek units that have been built is given in Table A-2.1.

Process Characteristics:

1. Scale of Operation: Commercial
2. Heat Supply: Autothermic
3. Flow: Concurrent
4. Gasifying Media: Steam, Oxygen

5. Ash Removal: Molten Slag, Continuous, 30 to 50% Bottom Ash Removal
6. Pressure: Slight Positive Pressure
7. Temperature: 2700 to 3500$^{\circ}$F
8. Product Gas: 300 Btu/SCF

Raw Gas Analysis of Major Components (dry basis) - Volume %:

| | Western Coal | Illinois Coal | Eastern Coal |
|---|---|---|---|
| CO | 58.68 | 55.38 | 55.90 |
| $CO_2$ | 7.04 | 7.04 | 7.18 |
| $H_2$ | 32.86 | 34.62 | 35.39 |
| $N_2$ | 1.12 | 1.01 | 1.14 |
| $H_2S$ | 0.28 | 1.83 | 0.35 |
| COS | 0.02 | 0.12 | 0.04 |

Dried Feed Coal Analysis, Weight %:

| | Western Coal | Illinois Coal | Eastern Coal |
|---|---|---|---|
| C | 56.76 | 61.94 | 69.88 |
| H | 4.24 | 4.36 | 4.90 |
| N | 1.01 | 0.97 | 1.37 |
| S | 0.67 | 4.88 | 1.08 |
| O | 13.18 | 6.73 | 7.05 |
| Ash | 22.14 | 19.12 | 13.72 |
| Moisture | 2.00 | 2.00 | 2.00 |

Koppers-Totzek Reference #2: Farnsworth, J.F.

## TABLE A-2.1

## GASIFICATION PLANTS USING THE K-T PROCESS

| Location | Number of Gasifier Units | Capacity: CO + $H_2$ in 24 Hours | Year of Order |
|---|---|---|---|
| Charbonnages de France,<br>Paris, France | 1 | 75,000-<br>150,000 $Nm^3$<br>2,790,000-<br>5,580,000 SCF | 1949 |
| Typpi Oy, Oulu<br>Finland | 3 | 140,000 $Nm^3$<br>5,210,000 SCF | 1950 |
| Nihon Suiso Kogyo Kaisha, Ltd.<br>Tokyo, Japan | 3 | 210,000 $Nm^3$<br>7,820,000 SCF | 1954 |
| Nitrogen Works in Puentes de<br>Garcia Rodriquez, Coruña, Spain | 3 | 242,000 $Nm^3$<br>9,000,000 SCF | 1954 |
| Typpi Oy, Oulu<br>Finland | 2 | 140,000 $Nm^3$<br>5,210,000 SCF | 1955 |
| S.A. Union Chimique Belge,<br>Brussels, Belfium | 2 | 176,000 $Nm^3$<br>6,550,000 SCF | 1955 |
| Amoniaco Português S.A.R.L.,<br>Lisbon, Portugal | 2 | 169,000 $Nm^3$<br>6,300,000 SCF | 1956 |
| Government of the Kingdom of Greece<br>Ptolemais, Greece | 4 | 629,000 $Nm^3$<br>23,450,000 SCF | 1959 |
| Nitrogen Works in Puentes de<br>Garcia Rodriquez, Coruña, Spain | 1 | 175,000 $Nm^3$<br>6,500,000 SCF | 1961 |
| Nitrogen Works of Société el Nasr d'Engrais<br>et d'Industries Chimiques, Attaka, Suez<br>United Arabian Republique | 3 | 778,000 $Nm^3$<br>28,950,000 SCF | 1963 |
| Chemical Fertilizer Company Ltd.,<br>Mae Moh, Lampang, Thailand | 1 | 217,000 $Nm^3$<br>8,070,000 SCF | 1963 |
| Azot Sanayii T.A.S., Ankara,<br>Kütahya Works, Turkey | 4 | 775,000 $Nm^3$<br>28,850,000 SCF | 1966 |

## TABLE A-2.1 (Cont'd)

| Location | Number of Gasifier Units | Capacity: $CO + H_2$ in 24 Hours | Year of Order |
|---|---|---|---|
| Chemieanlagen Export-Import G.m.b.H., Berlin für VEB Germania, Chemieanlagen und Apparatebau, Karl-Marx-Stadt, Germany | 2 | 360,000 $Nm^3$<br>13,400,000 SCF | 1966 |
| Kobe Steel Ltd., Zambia, Africa | 1 | 214,320 $Nm^3$<br>7,980,000 SCF | 1967 |
| Nitrogenous Fertilizers Industry S.A., Athens, Ptolemais, Greece | 1 | 165,000 $Nm^3$<br>6,150,000 SCF | 1968 |
| The Fertilizer Corporation of India Ltd., New Delhi, Ramagundam Plant, India | 4<br>(1 of them as stand-by) | 2,000,000 $Nm^3$<br>74,450,000 SCF | 1969 |
| The Fertilizer Corporation of India Ltd., New Delhi, Talcher Plant, India | 4<br>(1 of them as stand-by) | 2,000,000 $Nm^3$<br>74,450,000 SCF | 1970 |
| Nitrogenous Fertilizers Industry S.A., Athens Nitrogenous Fertilizers Plant Ptolemais, Greece | 1 | 242,000 $Nm^3$<br>9,009,000 SCF | 1970 |
| The Fertilizer Corporation of India Ltd., New Delhi, Korba Plant, India | 4<br>(1 of them as stand-by) | 2,000,000 $Nm^3$<br>74,450,000 SCF | 1972 |
| AE & CI Ltd., Johannesburg, Modderfontein Plant, South Africa | 6 | 2,150,000 $Nm^3$<br>80,025,000 SCF | 1972 |
| Indeco Chemicals Ltd., Lusaka, Kafue Works, Zambia | 1 | 220,800 $Nm^3$<br>8,220,000 SCF | 1974 |
| Indeco Chemicals Ltd., Lasaka, Kafue Works, Zambia | 2 | 441,600 $Nm^3$<br>16,440,000 SCF | 1975 |

## A.3 Lurgi Process

The Lurgi producer is a moving-bed, intermediate pressure gasifier with counter-current flow of coal and gas. Dry ash is removed from the bottom and gas exits from near the top.

Coal of 1/4 to 1-3/4 inch is fed to the top of the gasifier through a pressurized lock hopper. Fine coal particles are not acceptable in the feed; large particles are needed to permit sufficient gas passage. The coal, ideally nonagglomerating, flows downward through the moving-bed gasifier. A rabble arm levels the coal on the surface of the bed.

Steam and air or oxygen are introduced at the bottom of the reactor through a revolving grate; as these gases rise through the reaction zone, they react with residual carbon to produce heat necessary to carry out the gasification reactions. To insure complete gasification, a sufficiently high temperature must be maintained by control of the steam/oxygen ratio. This temperature must be below the ash fusion point but high enough to provide the heat necessary in the endothermic gasification zone.

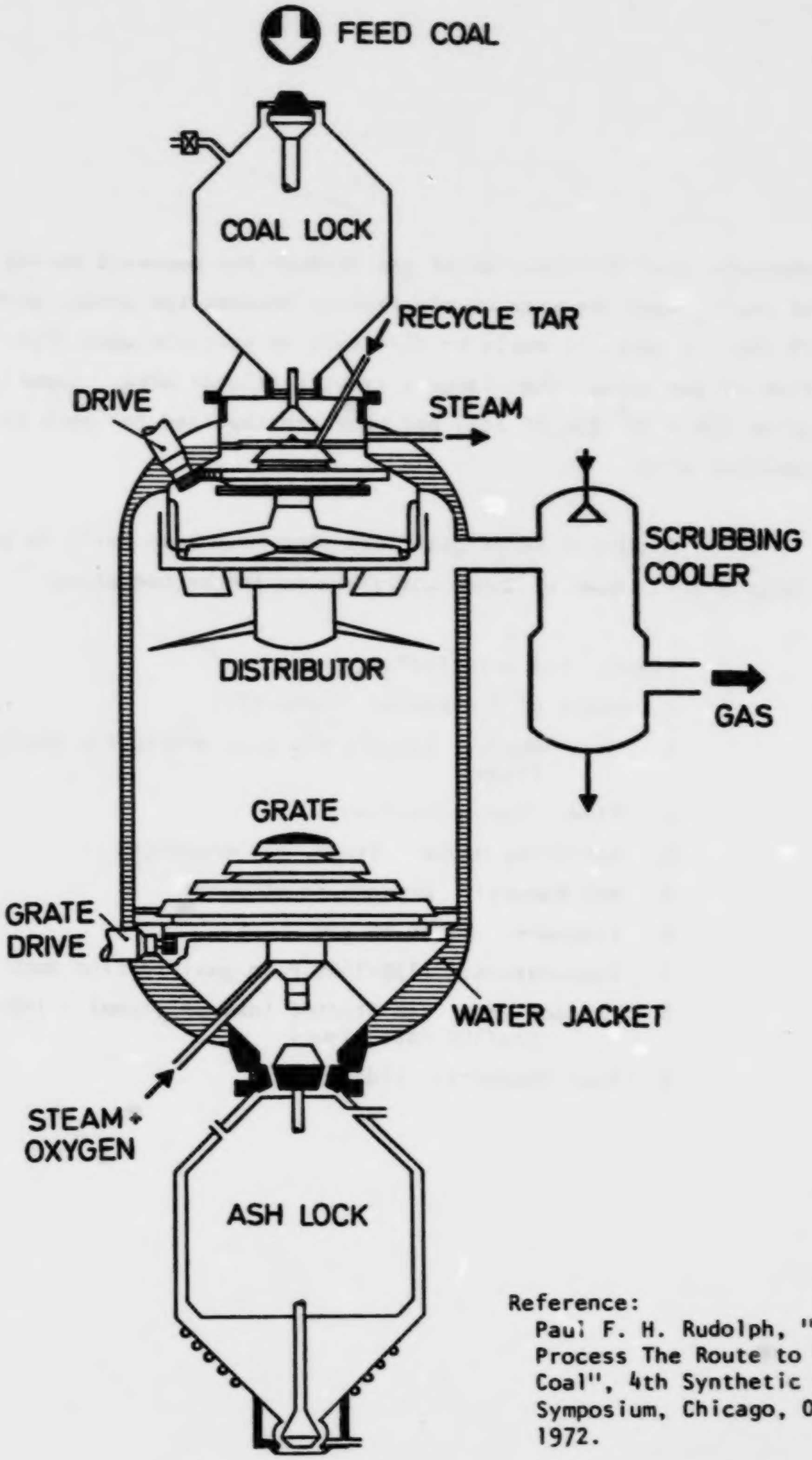
The moving bed has a layered temperature profile, which increases as the coal proceeds downward until reaching approximately 2000°F in the bottom combustion zone. At the top of the bed, feed coal is preheated, dried, and heated up to start devolatilization. Carbonization products, such as tar, oils, naphtha, light hydrocarbons, phenols and ammonia, together with a mixture of hydrogen and carbon monoxide are produced starting at about 900°F to 950°F. From a temperature of 1150°F to 1400°F onward, devolatilization is accompanied by gasification of the resulting char. The kinetics of the devolatilization and gasification reactions is related to the reactivity of the coal and, thus, the minimum temperature at which the reaction will proceed. The approximate final reaction temperatures at which the reaction rates of various coals approach zero are:

| | |
|---|---|
| Lignite | 1200°F |
| Sub-bituminous | 1350°F |
| Semi-anthracite | 1450°F |
| Coke | 1550°F |

To achieve a good performance of the reactions, the minimum required residence time of a coal grain at the desired temperature level of 1400°F to 1600°F is about one hour.

Gas leaving the bed contains, in addition to the carbonization products, coal and ash particulates plus some hydrogen sulfide and carbonyl sulfides. The exiting gas temperature is at 700°F to 1100°F depending on the type of coal.

The relatively uncomplicated Lurgi gasifier design shown in Figure A-3.1 utilizes a double-walled vessel with hot water or boiling water between the walls. Gasifiers of recent design are not internally insulated. The Lurgi design incorporates a mechanically-driven grate at the bottom of the gasifier. The grate supports the fuel bed, removes the ash into a lock hopper, and allows introduction of steam and air to the gasifier. The ash, a granular, low-carbon material, is discharged from the pressure reactor through an ash lock chamber. The literature indicates the physical limit to the diameter of Lurgi gasifiers has been established by the need to


FEED COAL
COAL LOCK
RECYCLE TAR
DRIVE
STEAM
SCRUBBING COOLER
DISTRIBUTOR
GAS
GRATE
GRATE DRIVE
WATER JACKET
STEAM + OXYGEN
ASH LOCK

Reference:
Paul F. H. Rudolph, "The Lurgi Process The Route to SNG from Coal", 4th Synthetic Pipeline Gas Symposium, Chicago, Oct. 30 & 31, 1972.

LURGI PRESSURE GASIFIER

FIGURE A-3.1

maintain good distribution of gas through the downward moving bed of coal. When the size of the reactor becomes too great, perhaps 15 feet or more, it would be difficult to maintain good distribution of gas across that large a cross-sectional area. Capacities up to 570 x $10^6$ Btu of coal per hour are reported for each Lurgi gasifier unit.

A list of Lurgi gasifiers that have been built is given in Table A-3.1. Some of these units are no longer operating.

Process Characteristics:

1. Scale of Operation: Commercial
2. Heat Supply: Autothermic with externally heated steam
3. Flow: Counter-current
4. Gasifying Media: Steam, air or oxygen
5. Ash Removal: Dry-ash, continuous
6. Pressure: 10 to 30 atm.
7. Temperature: 1150-1600°F in gasification zone
8. Product Gas: 310 Btu/SCF (oxygen-blown) - 140-180 Btu/SCF (air blown)
9. Heat Recovery: Side wall

## TABLE A-3.1

## LIST OF LURGI GASIFIERS*

| Plant No. | Location | Year | Type of Coal | Gasifier I.D. | Capacity (MM SCFD) | No. of Gasifiers |
|---|---|---|---|---|---|---|
| 1 | Hirschfelde, Central Germany | 1936 | Lignite | 3'9" | 1.1 | 2 |
| 2 | Bohlen, Central Germany | 1940 | Lignite | 8'6" | 9.0 | 5 |
| 3 | Bohlen, Central Germany | 1943 | Lignite | 8'6" | 10.0 | 5 |
| 4 | Most, CSSR | 1944 | Lignite | 8'6" | 7.5 | 3 |
| 5 | Zaluzi-Most, CSSR | 1949 | Lignite | 8'6" | 9.0 | 3 |
| 6 | Sasolburg, South Africa | 1954 | Sub-Bitum. with 30% ash and more | 12'1" | 150.0 | 9 |
| 7 | Dorsten, West Germany | 1955 | Caking Sub-Bitum. with high chlorine content | 8'9" | 55.0 | 6 |
| 8 | Morwell, Australia | 1956 | Lignite | 8'9" | 22.0 | 6 |
| 9 | Daud Khel, Pakistan | 1957 | High volatile coal with high sulfur content | 8'9" | 5.0 | 2 |
| 10 | Sasolburg, South Africa | 1958 | Sub-Bitum. with 30% ash and more | 12'1" | 19.0 | 1 |
| 11 | Westfield, Great Britain | 1960 | Weakly Caking Sub-Bitum. | 8'9" | 28.0 | 3 |
| 12 | Jealgora, India | 1961 | Different grades | N/A | 0.9 | 1 |
| 13 | Westfield, Great Britain | 1962 | Weakly Caking Sub-Bitum. | 8'9" | 9.0 | 1 |
| 14 | Coleshill, Great Britain | 1963 | Caking Sub-Bitum. with high chlorine content | 8'9" | 46.0 | 5 |
| 15 | Naju, Korea | 1963 | Graphitic anthracite with high ash content | 10'5" | 15.0 | 3 |
| 16 | Sasolburg, South Africa | 1966 | Sub-Bitum. with 30% ash and more | 12'1" | 75.0 | 3 |
| 17 | Luenen, GFR | 1970 | Sub-Bitum. | 11'4" | 1400 MM Btu/hr | 5 |
| 18 | Sasolburg, South Africa | 1973 | Sub-Bitum. with 30% ash and more | 12'4" | 190.0 | 3 |

* Some units are no longer in operation.

Typical Gas Compositions of Major Components (dry basis) - Volume %:

| Gas Components | Rhenish Brown Coal | | S. African Bituminous Coal | | S. African Bituminous Coal (Air-blown) |
|---|---|---|---|---|---|
| | Raw Gas | Purified(1) | Raw Gas | Purified(2) | Raw Gas |
| $CO_2$ | 32.2 | 2.0 | 30.2 | 1.0 | 15-17 |
| $H_2S$ | 0.1 | -- | 0.3 | -- | 0.2 |
| $C_n H_m$ | 0.5 | 0.5 | 0.2 | -- | 0.5 |
| CO | 17.4 | 25.2 | 17.4 | 24.9 | 15 |
| $H_2$ | 37.2 | 54.0 | 42.0 | 60.0 | 24 |
| $CH_4$ | 12.1 | 17.6 | 9.4 | 13.4 | 6 |
| $N_2$ | 0.5 | 0.7 | 0.5 | 0.7 | 40-45 |
| Gross Heating Value, Btu/SCF | 300 | 435 | 290 | 405 | 140-170 |
| Fuel Coal, W %: | | | | | |
| Moisture (3) | | 20.20 | | 10.50 | 10.50 |
| Ash | | 4.65 | | 21.76 | 21.76 |
| Fixed Carbon | | 35.40 | | 44.45 | 44.45 |
| Volatile Matter | | 39.75 | | 23.29 | 23.29 |
| Sulfur, Combustible | | 0.28 | | 0.75 | 0.75 |

NOTES:
1) After purification to remove acid gas by unspecified process.
2) After purification to remove acid gas by Rectisol process.
3) Some coals fed to the Lurgi reactor may contain up to 30-35% moisture.

Lurgi Reference #7: Lowry, H.H.

## A.4 Riley-Morgan Process

The Riley-Morgan gas producer is a low-pressure (up to 40 inches of water gauge), stirred moving-bed gasifier. The new design is an improved version of the old Morgan gas producers of which over 9,000 were sold through the 1940's. Improvements included replacing castings with weldments, an outer gas and dust tight casing for personnel protection, water seals for higher operating pressure, increased volume to handle the swelling tendency of certain coals, a water-cooled agitator to handle caking coals, and automated controls to reduce the number of operating personnel.

Coal of 1/4 to 1-1/2 inch is fed to the top of the gasifier. Both noncaking and caking coals can be gasified because the deep bed agitator can break up agglomerated masses.

The fuel bed is supported on an ash bed which, in turn, is supported on a rotating ash pan. The pan, barrel and charge all rotate together. The fuel bed is smoothed out by leveler arms and moves downward as the gasification of fuel proceeds. As the ash level becomes too high, ash is moved by a helical plow from the bottom of the gasifier.

Steam and air or oxygen are fed to the bottom of the gasifier. Air is brought in without a fan by an injection system which mixes and inducts air by steam flow in venturis.

Gases leave the top of the reactor, pass through a cyclone to remove dust, and are cooled first in an air condenser and then in a water condenser. Cooler condensate is separated from the gas which proceeds on to further processing as required by downstream gas utilization.

A Riley-Morgan unit is shown in Figure A-4.1.

A sulfur and a nitrogen balance for the Riley-Morgan system is given in Appendix C.

Process Characteristics:

1. Scale of Operation: Two years full scale laboratory test
2. Heat Supply: Autothermic
3. Flow: Counter-current
4. Gasifying Media: Steam, air or oxygen (proposed)
5. Ash Removal: Dry ash, intermittent
6. Pressure Atmospheric
7. Product Gas: 305 Btu/SCF (oxygen-blown) - 160 Btu/SCF (air-blown)

Raw Gas Analyses of Major Components (dry basis and sulfur-free basis) Volume %:

| | Air-Blown | Oxygen-Blown |
|---|---|---|
| CO | 26.0 | 41.2 |
| $H_2$ | 18.0 | 38.9 |
| $CH_4$ | 1.4 | 2.8 |
| $CO_2$ | 3.8 | 15.9 |
| $C_nH_m$ | 0.2 | 0.7 |
| $N_2$ | 50.0 | 0.5 |

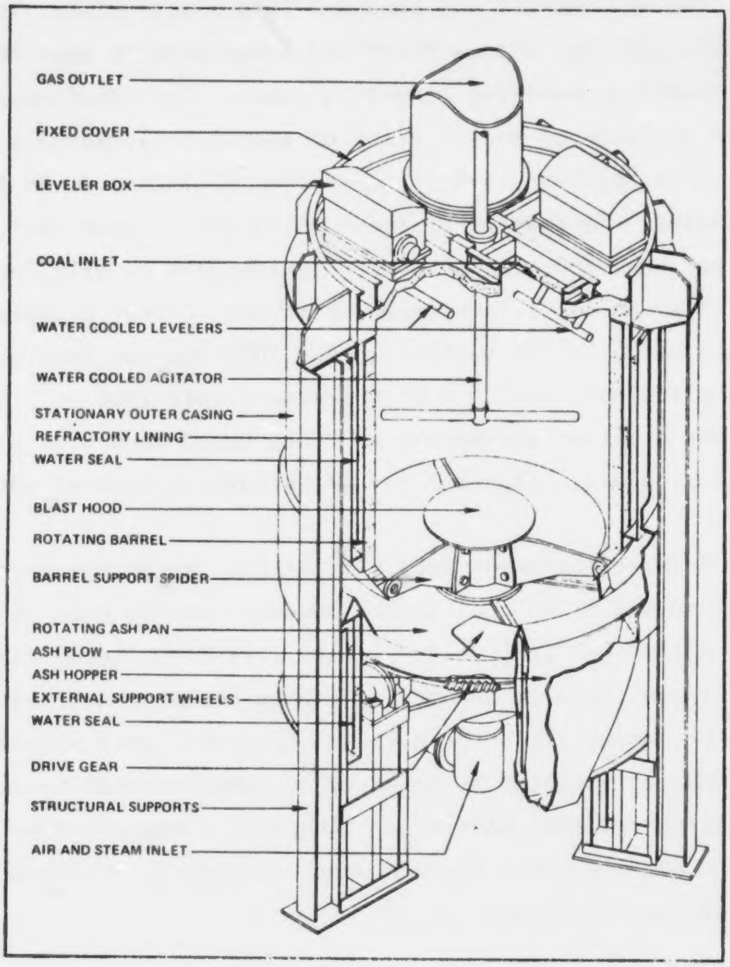
Approximate Analysis of Feed Coal (U.S. Eastern Bituminous Coal):

| | |
|---|---|
| Moisture | 7.2% |
| Volatile Matter | 34.4% |
| Fixed Carbon | 42.7% |
| Ash | 15.7% |

Riley-Morgan Reference #3: Rawdon, A.H., et al.

FIGURE A-4.1

## RILEY-MORGAN GAS PRODUCER



GAS OUTLET
FIXED COVER
LEVELER BOX
COAL INLET
WATER COOLED LEVELERS
WATER COOLED AGITATOR
STATIONARY OUTER CASING
REFRACTORY LINING
WATER SEAL
BLAST HOOD
ROTATING BARREL
BARREL SUPPORT SPIDER
ROTATING ASH PAN
ASH PLOW
ASH HOPPER
EXTERNAL SUPPORT WHEELS
WATER SEAL
DRIVE GEAR
STRUCTURAL SUPPORTS
AIR AND STEAM INLET

Reference: Riley-Morgan Brochure

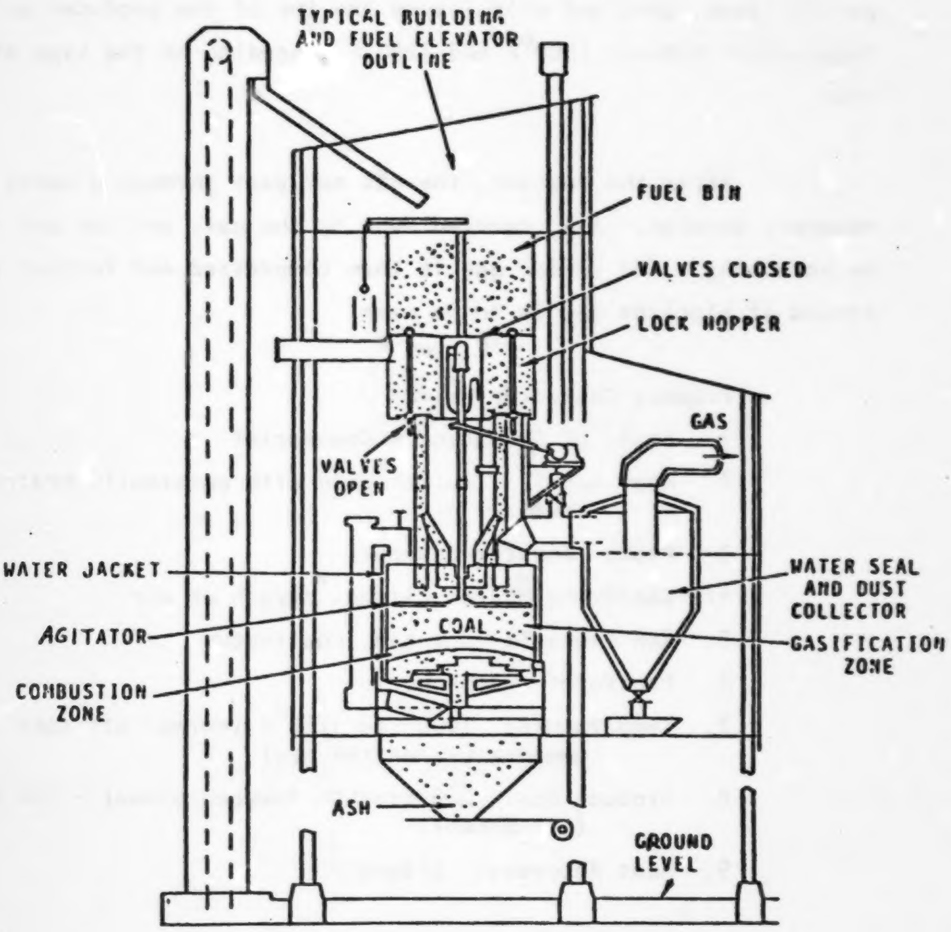
## A.5 Wellman-Galusha Process

The Wellman-Galusha producer is a single-stage, low-temperature, low-pressure gasifier with a fixed bed through which coal moves slowly downward toward a revolving eccentric grate. Gas flows upward countercurrent to the flow of coal. Sizes of the water jacketed automatic producers with revolving grates range from 42 inches to 10 feet in inner diameter. Capacities of these units are, respectively, 192 to 1600 lbs per hour (40 million Btu/hr) using 3/16 to 5/16 inch anthracite. With an agitator, the capacity of the 10 feet diameter unit is 2000 lbs per hour for anthracite and 7000 lbs per hour on 1-1/4 to 2 inch bituminous coal. A high pressure unit (300 psi) has been designed and built at the Bureau of Mines Research Center in Morgantown, West Virginia. Figure A-5.1 illustrates a typical unit.

A two-compartment fuel bin, at the top of the producer, feeds crushed and dried coal to the downward moving bed. A slowly revolving horizontal arm, which spirals vertically below the surface of the fuel bed, retards channeling and maintains a uniform bed. The producer can gasify anthracite and coke but, when bituminous coal is used, an agitator is required to avoid channeling and caking (agglomerating) of coal particles. The bed is supported by a slowly revolving eccentric grate through which dry ash is continuously ejected into an ash hopper.

Gas flow is upward through the gasifier. Steam, generated in the water jacket surrounding the gasifier, and air or oxygen are introduced through the revolving grate. Depending on the type of gas required, $CO_2$ can be substituted for the steam. This procedure would avoid formation of hydrogen from the steam in order to make

FIGURE A-5.1


TYPICAL BUILDING AND FUEL ELEVATOR OUTLINE
FUEL BIN
VALVES CLOSED
LOCK HOPPER
GAS
VALVES OPEN
WATER JACKET
WATER SEAL AND DUST COLLECTOR
AGITATOR
COAL
GASIFICATION ZONE
COMBUSTION ZONE
ASH
GROUND LEVEL

WELLMAN-GALUSHA FUEL GAS GENERATOR

Reference: Wellman-Galusha Brochure

a gas with improved burning characteristics. Raw gas containing particulates, tars and oils leaves the top of the producer at a temperature between 1000°F and 1250°F depending on the type of coal.

After the reactor, the gas may pass through a waste heat recovery section. Ash, carried over by the gas, and tar are removed by scrubbing. The cooled gas is then compressed and further processed if pipeline gas is to be made.

Process Characteristics:

1. Scale of Operation: Commercial
2. Heat Supply: Autothermic with externally heated steam
3. Flow: Counter-current
4. Gasifying Media: Steam, oxygen or air
5. Ash Removal: Dry-ash, continuous
6. Pressure: Atmospheric
7. Temperature: 1000° to 1250°F (normal off-take temperature of the gas)
8. Product Gas: 260 Btu/SCF (oxygen-blown) - 160 Btu/SCF (air-blown)
9. Heat Recovery: Sidewall

Raw Gas Analysis of Major Components (Unspecified Coal):

| Component | Mol % High-Btu | Mol % Low-Btu |
|---|---|---|
| CO | 29.6 | 26.0 |
| $CO_2$ | 12.3 | 3.0 |
| $H_2$ | 30.3 | 13.9 |
| $H_2O$ | 25.3 | 8.3 |
| $CH_4$ | 0.7 | 2.5 |
| $N_2$ | 1.1 | 45.6 |
| $O_2$ | 0.1 | |
| $H_2S$/COS | 0.6 | 0.7 |
| Total | 100.0 | 100.0 |

Higher Heating Value
(dry basis), Btu/SCF 268

General Reference #1

Raw Gas Analysis of Major Components (dry and sulfur-free basis)

Volume %:

| | Anthracite PA | Coke | Bituminous A W. Va. |
|---|---|---|---|
| $H_2$ | 41.0 | 31.0 | 15.0 |
| $O_2$ | 0.1 | 0.6 | -- |
| $CO$ | 40.0 | 54.1 | 28.6 |
| $CO_2$ | 16.5 | 11.3 | 3.4 |
| $CH_4$ | 0.9 | 0.4 | 2.7 |
| $N_2$ | 1.5 | 2.6 | 50.3 |

Feed Coal:

| | Anthracite PA | Coke | Bituminous A W. Va. |
|---|---|---|---|
| Proximate Analysis, W% | | | |
| Moisture | 6.4 | 5.0 | 3.7 |
| Ash | 10.2 | 11.9 | 3.5 |
| Volatile Matter | 4.5 | -- | 36.3 |
| Fixed Carbon | 78.9 | 83.1 | 56.5 |
| Ultimate Analysis, W% | | | |
| C | 78.7 | 84.1 | |
| H | 2.4 | 1.8 | |
| N | 0.7 | 0.8 | |
| O | 7.4 | 1.8 | |
| S | 0.6 | 0.6 | |
| Ash | 10.2 | 10.9 | |

Wellman-Galusha References #3 and #7.

## A.6 Wilputte Process

The Wilputte producer is a moving-bed gasifier, operating at atmospheric pressure. The producer is equipped with a rotating grate and ash pan assembly which rests on roller supports. A stationary ash plow removes the ash from the ash pan and discharges the ash into an ash trough. The producer is supported above the rotating grate and ash pan assembly by columns from the floor and is sealed by water in the ash pan. The producer can gasify either bituminous or lignite coal with air or oxygen. A rotating rabble arm (agitator) is used to mix and break up the agglomerates when a caking coal is gasified.

The crushed coal of less than 4 inches is fed through the top of the gasifier. Moist air or oxygen flows upward through a rotating grate. The fresh coal is pyrolyzed to expel volatile hydrocarbon products at the upper portion of the fuel bed, and the carbon residue from pyrolyzed coal is burned and gasified with air and steam to carbon dioxide, carbon monoxide and hydrogen. The product gas leaves the producer at about 1100-1200$^{\circ}$F.

The raw product gas contains coal tar, light oil, hydrogen sulfide and particulates. The gas is passed through a cyclonic dust collector to a waste heat boiler that lowers the temperautre of the gas stream to about 800$^{\circ}$F. The gas is then quenched with an aqueous liquor and further scrubbed with the liquor in a packed tower to remove light oil, tar and particulates. When operating on a low-sulfur coal, the scrubbed gas can be used at this point as a fuel without additional processing. If high-sulfur coal is used, or complete sulfur removal is required, the gas stream is further purified by a secondary scrubber and by an electrostatic precipitator before entering the sulfur removal system. The Holmes-Stretford process may be used for the removal of hydrogen sulfide. A system to remove HCN from the gas stream prior to entry into the Holmes-Stretford unit is not required because the HCN content of the gas is so low that fouling of the absorbent solution with thiocyanates is not a serious problem.

The heating value of the producer gas is affected by the volatile content of the feed material. Bituminous coal and lignites will produce a fuel gas with a heating value of 160-170 Btu/SCF. The HHV of gas from anthracite or coke will be somewhat lower.

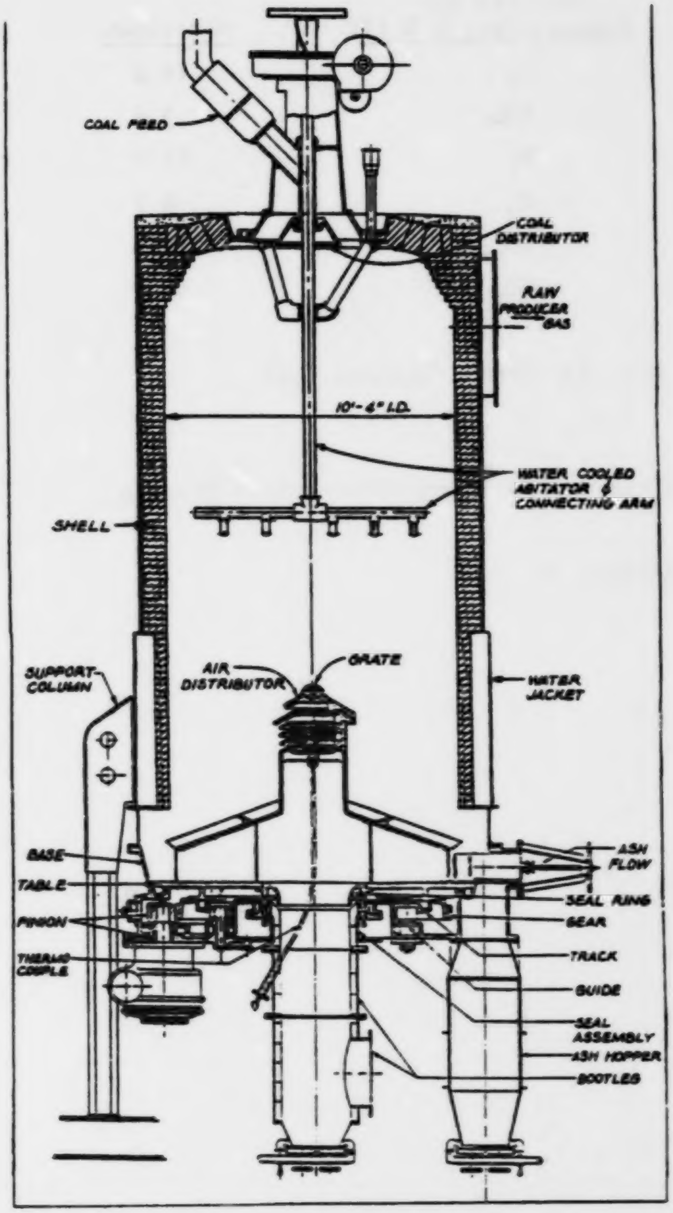
Process Characteristics:

1. Scale of Operation - Commercial
2. Heat Supply - Autothermic
3. Flow - Counter-current
4. Gasifying Media - Moist air or oxygen
5. Ash Removal - Dry ash, continuous
6. Pressure - Atmospheric
7. Product Gas - 165 Btu/SCF (air-blown) - 300 Btu/SCF (oxygen-blown)
8. Heat Recovery - Sidewall

A Wilputte gasifier is illustrated in Figure A-6.1.

FIGURE A-6.1

WILPUTTE GASIFIER


COAL FEED
COAL DISTRIBUTOR
RAW PRODUCER GAS
10'-4" I.D.
WATER COOLED AGITATOR & CONNECTING ARM
SHELL
SUPPORT-COLUMN
AIR DISTRIBUTOR
GRATE
WATER JACKET
BASE
TABLE
PINION
THERMO COUPLE
ASH FLOW
SEAL RING
GEAR
TRACK
GUIDE
SEAL ASSEMBLY
ASH HOPPER
BOOTLEG

Reference: Wilputte Co. Brochure

| Purified Gas Composition, V % (1) | Air-blown |
|---|---|
| $H_2$ | 16.6 |
| $CH_4$ | 3.6 |
| $N_2$ | 51.0 |
| $O_2$ | 0.2 |
| CO | 22.7 |
| $CO_2$ | 5.9 |

Feed Coal: U.S. Eastern Bituminous Coal.

NOTE: 1) After Purification by Stretford Process

Wilputte Reference #1

## A.7 Winkler Process

The Winkler producer is a fluidized-bed gasifier, operating at low (up to 3 psig) pressure. The Winkler generator was initially designed to make producer gas from coal with air and steam gasification. The gas was used as an industrial fuel for both direct combustion and use in stationary internal combustion engines. A proposed recent version of the Winkler gasifier has been designed to operate at a pressure of about 125 psi. Operation at this proposed pressure level is said to improve the economics of both the oxygen-blown and the air-blown models of this system.

Coal is normally crushed in the range of 0 to 3/8-inch and dried. Past operating experience has indicated that the coal feed need be dried only if surface moisture is present and the coal cannot be handled without plugging screens, conveyors, etc. Generally, coals with moisture contents of up to 18% can be handled and gasified without drying.

Coal enters the producer through a variable-speed screw feeder. The screws, in addition to providing control on the coal feed rate, serve to seal the producer preventing steam from wetting the coal feed and blocking the feed line.

The primary supply of steam and oxygen (or air) enters the bottom of the gasifier. Coal reacts with oxygen and steam to produce a gas rich in carbon monoxide and hydrogen. A secondary blast of steam and oxygen or air above the fluidized bed converts unreacted carbon in the gas-entrained particles and raises the bed to maximum temperature.

Gasification reactions in the Winkler gasifier are primarily a combination of combustion and water-gas reaction at temperatures of 1500°F to 2000°F depending on the type of coal. The high temperature reacts all tars and heavy hydrocarbons. Before leaving the gasifier, the gas is cooled by a radiant heat boiler section to prevent ash particles from melting and forming deposits in the exit duct.

As a result of high fluidization gas velocity, the ash particles are segregated according to size and specific gravity. The larger, heavier ash particles fall down through the fluidized bed and pass into the ash discharge unit at the bottom of the gasifier while the lighter particles are carried up and out of the fuel bed by the product gas. Experience has shown that approximately 30% of the ash leaves at the bottom while 70% is carried overhead. An auxiliary unit provides a hot bed of coal for initial start-up.

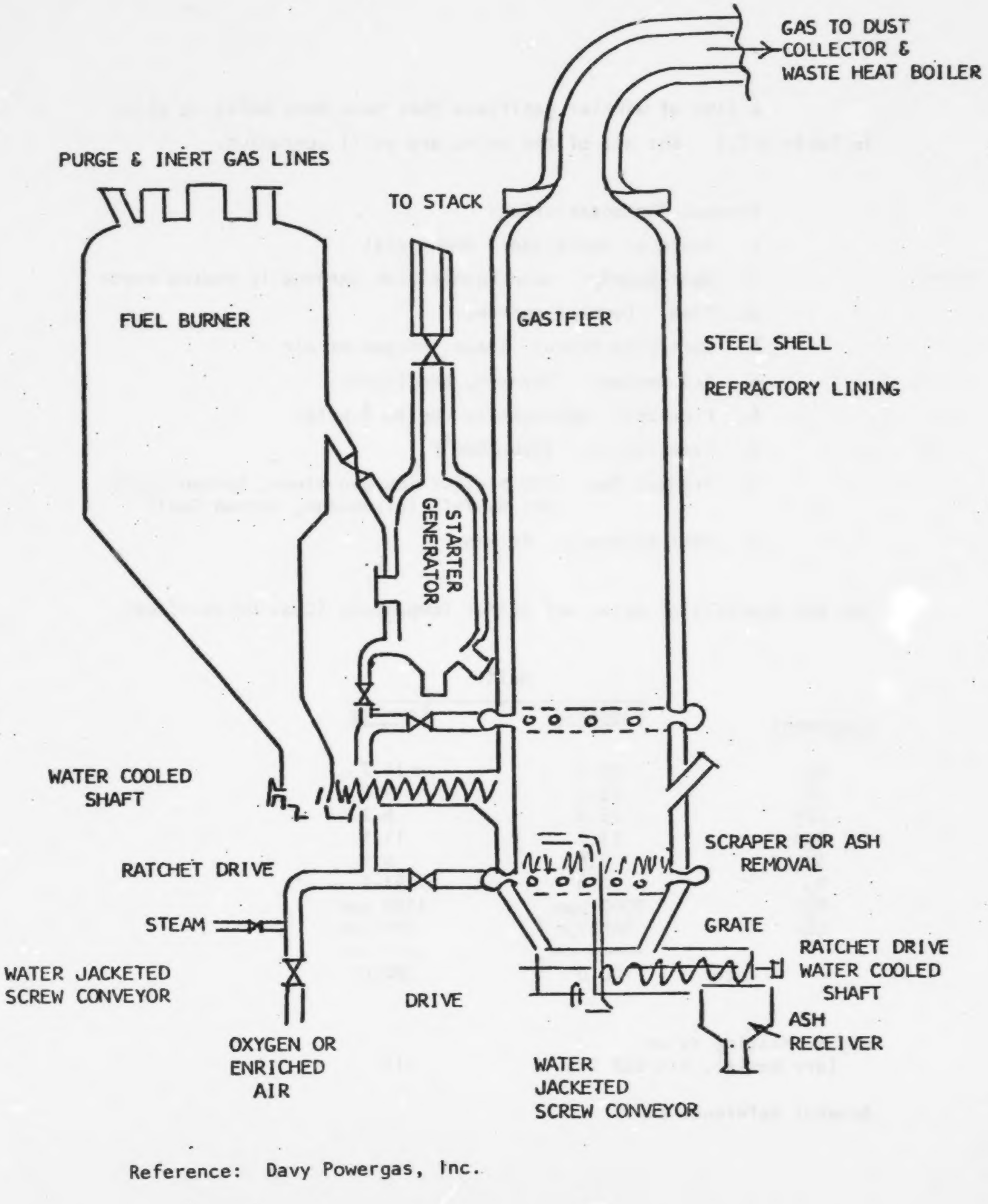
Raw gas leaving the gasifier is passed through a further waste heat recovery section. Fly ash is removed by cyclones followed by a wet scrubber and finally, if appropriate for the application, an electrostatic precipitator. The gas may then be compressed and shifted if continuing on to pipeline gas. The gas coming from the shift converter is purified, methanated, dehydrated, and compressed further if necessary to produce pipeline quality.

The ash removed in the dry state is conveyed pneumatically to an ash bunker. That which is removed wet is recovered as a slurry in a settler and then mixed with the warm dry ash where the contained water cools the ash and wets it to prevent dusting problems during ultimate disposal.

A Winkler unit is shown in Figure A-7.1.

FIGURE A-7.1

A WINKLER GASIFIER


GAS TO DUST
COLLECTOR &
WASTE HEAT BOILER
PURGE & INERT GAS LINES
TO STACK
FUEL BURNER
GASIFIER
STEEL SHELL
REFRACTORY LINING
STARTER
GENERATOR
WATER COOLED
SHAFT
SCRAPER FOR ASH
REMOVAL
RATCHET DRIVE
STEAM
GRATE
RATCHET DRIVE
WATER COOLED
SHAFT
WATER JACKETED
SCREW CONVEYOR
DRIVE
ASH
RECEIVER
OXYGEN OR
ENRICHED
AIR
WATER
JACKETED
SCREW CONVEYOR

Reference: Davy Powergas, Inc.

A list of Winkler gasifiers that have been built is given in Table A-7.1. Not all of the units are still operating.

Process Characteristics:

1. Scale of Operation: Commercial
2. Heat Supply: Autothermic with externally heated steam
3. Flow: Counter-current
4. Gasifying Media: Steam, oxygen or air
5. Ash Removal: Dry-ash, continuous
6. Pressure: Atmospheric (up to 8 psig)
7. Temperature: 1500-2000°F
8. Product Gas: 270 Btu/SCF (oxygen-blown, German Coal)
   105 Btu/SCF (air-blown, German Coal)
9. Heat Recovery: External

Raw Gas Analysis of Major and Sulfur Components (Coal Unspecified):

| Component | Mol% High-Btu | Mol% Low-Btu |
|---|---|---|
| $H_2$ | 32.2 | 11.7 |
| CO | 25.7 | 19.0 |
| $CO_2$ | 15.8 | 6.2 |
| $H_2O$ | 23.1 | 11.5 |
| $CH_4$ | 2.4 | 0.5 |
| $N_2$ | 0.8 | 51.1 |
| $H_2S$ | 2500 ppm | 1300 ppm |
| COS | 400 ppm | 200 ppm |
| Total | 100.0 | 100.0 |
| Higher Heating Value (dry basis), Btu/SCF | 275 | 118 |

General Reference #1

Raw Gas Analysis of Major Components (dry basis) - Volume %:

| | Oxygen-Blown |
|---|---|
| $H_2$ | 38.5 |
| $CO$ | 35.3 |
| $CO_2$ | 21.8 |
| $CH_4$ | 1.8 |
| $N_2$ | 1.1 |
| $H_2S$ | 1.5 |

Ultimate Analysis of Feed Coal (German Brown Coal):

| | W % |
|---|---|
| Moisture | 8.0 |
| Ash | 15.4 |
| C | 54.6 |
| H | 4.1 |
| N | 0.6 |
| S | 3.3 |
| O | 14.0 |

Winkler Reference #4.

TABLE A-7.1

## PLANT LIST - WINKLER GENERATORS

| Plant No. | Plant | Year | Product | Capacity Per Generator | | | | No. Gen. |
|---|---|---|---|---|---|---|---|---|
| | | | | Normal | | Maximum | | |
| | | | | 1000 NM$^3$/hr | 1000 SCFH | 1000 NM$^3$/hr | 1000 SCFH | |
| 1 | Leuna-Werk<br>Leuna, Germany | 1926-<br>1930 | Fuel Gas<br>Water Gas | 60<br>30 | 2240<br>1120 | 100<br>50 | 3730)<br>1870) | 5 |
| 2 | Braunkohle-Benzin AG<br>Bohlen, Germany | 1936 | Water Gas | 27.6 | 1030 | 30 | 1120 | 3 |
| 3 | Braunkohle-Benzin AG<br>Magdeburg, Germany | 1936 | Water Gas | 27.6 | 1030 | 33 | 1230 | 3 |
| 4 | Yahagi<br>Japan | 1937 | Water Gas | 8.75 | 330 | -- | -- | 1 |
| 5 | Braunkohle-Benzin AG<br>Zeitz, Germany | 1938 | Water Gas | 22.5 | 840 | -- | -- | 3 |
| 6 | Dai-Nihonyinzo-Hiryo<br>Japan | 1938 | Synthesis Gas | 14 | 520 | -- | -- | 2 |
| 7 | Nippon Tar<br>Japan | 1938 | Water Gas | 14 | 520 | -- | -- | 2 |
| 8 | Toyo-Koatsu<br>Japan | 1939 | Synthesis Gas | 15 | 560 | 20 | 750 | 2 |
| 9 | Sudetenlandische Treibstoffwerke<br>Brux, Czechoslovakia | 1943 | Water Gas | 27.6 | 1030 | 30 | 1120 | 5 |
| *10 | Fabrika Azotnih Jendinjenja<br>Gorazde, Yugoslavia | 1953 | Synthesis Gas | 5 | 190 | -- | -- | 1 |
| 11 | Calvo Sotelo<br>Puertollano, Spain | 1954 | Water Gas | 9.5 | 350 | -- | -- | 1 |
| 12 | Union Rheinische Braunkohlen<br>Wesseling, Germany | 1956 | Synthesis Gas | 12 | 450 | 17 | 630 | 1 |

(Continued)

TABLE A-7.1 (Cont'd)

| Plant No. | Plant | Year | Product | Capacity Per Generator<br>Normal<br>1000 $NM^3$/hr | <br><br>1000 SCFH | <br>Maximum<br>1000 $NM^3$/hr | <br><br>1000 SCFH | No. Gen. |
|---|---|---|---|---|---|---|---|---|
| 13 | Calvo Sotelo<br>Puertollano, Spain | 1957 | Synthesis Gas | 9.5 | 350 | -- | -- | 1 |
| *14 | Azot Sanyyii TAS<br>Kutahya, Turkey | 1959 | Synthesis Gas | 12 | 450 | 18 | 670 | 2 |
| *15 | Neyveli Lignite Corporation<br>Madras, India | 1959 | Synthesis Gas | 41.6 | 1550 | -- | -- | 3 |
| *16 | Union Reinische Braunkohlen<br>Wesseling, Germany | 1960 | Synthesis Gas | 12 | 450 | 17 | 630 | 1 |

* Presently operating

## A.8 Woodall-Duckham/Gas Integrale Process

The Woodall-Duckham/Gas Integrale process is a two-stage, moving-bed gas producer. The producer consists of a distillation retort surmounting a gasification shell. The producer is top fed, operating at atmospheric pressure with ash continuously withdrawn through a grate at the bottom of the producer. The lower portion of the producer is water jacketed and the upper portion is made of hollow refractory tile.

Coal of 3/4 to 2-3/4 inch is fed to the top of the producer and descends in the distillation retort (first stage) through gradually increasing temperature zones. All volatile matter is expelled until only carbon and ash (distillation coke) remain to enter the gasification zone (second stage).

In the gasification zone air and steam enter through a rotating grate at the base of the producer and the carbon in the distillation coke is gasified. A part of the hot producer gas (called clear gas) travels upward through the fresh coal in the upper portion of the producer while the sensible heat of the gas is used to distill off the volatile matter of the fresh coal. The producer gas mixes with distillation vapors to leave the retort as mixed gas at temperatures of $210^{\circ}F$ to $300^{\circ}F$. The mixed gas consists of 60-75% water gas ($CO$ & $H_2$), with the balance being coal distillation gas, tar, light oils and unreacted steam. The remaining part of the clear gas (a mixture of $CO$, $H_2$, $CO_2$, $CH_4$ and $N_2$ and completely free from oil and tar) leaves the gasifier through a blast gas outlet at a temperature of $800^{\circ}F$ to $1000^{\circ}F$. The producer cannot handle a highly caking coal.

Refer to Figure A-8.1 for a WD/GI illustration.

A list of WD/GI gasifiers is given in Table A-8.1.

Process Characteristics:

1. Scale of Operation: Commercial
2. Heat Supply: Autothermic
3. Flow: Counter-current
4. Gasifying Media: Steam, oxygen or air
5. Ash Removal: Dry-ash, continuous
6. Pressure: Atmospheric
7. Product Gas: 340 Btu/SCF (oxygen-block) - 175 Btu/SCF (air-blown)
8. Heat Recovery: Sidewall

Raw Gas Composition of Major Components (dry and sulfur-free) - Volume %:

| | Air-Blown | | |
|---|---|---|---|
| | Continuous | Cyclic | Oxygen-Blown |
| $H_2$ | 17.0 | 50-56 | 38.4 |
| $O_2$ | Nil | 0.1-0.3 | 0.0 |
| CO | 28.3 | 26-31 | 37.5 |
| $CO_2$ | 4.5 | 6-10 | 18.0 |
| $CH_4$ | | | 3.5 |
| $C_nH_m$ | 3.0 | 5-8 | 0.4 |
| $N_2$ | 47.2 | 2-6 | 2.2 |

Proximate Analysis of Coal, W%

| | |
|---|---|
| Moisture | 11.0 |
| Volatile Matter | 35.4 |
| Fixed Carbon | 44.9 |
| Ash | 8.7 |

Woodall Duckham/Gas Integrale References # 2 & # 3.

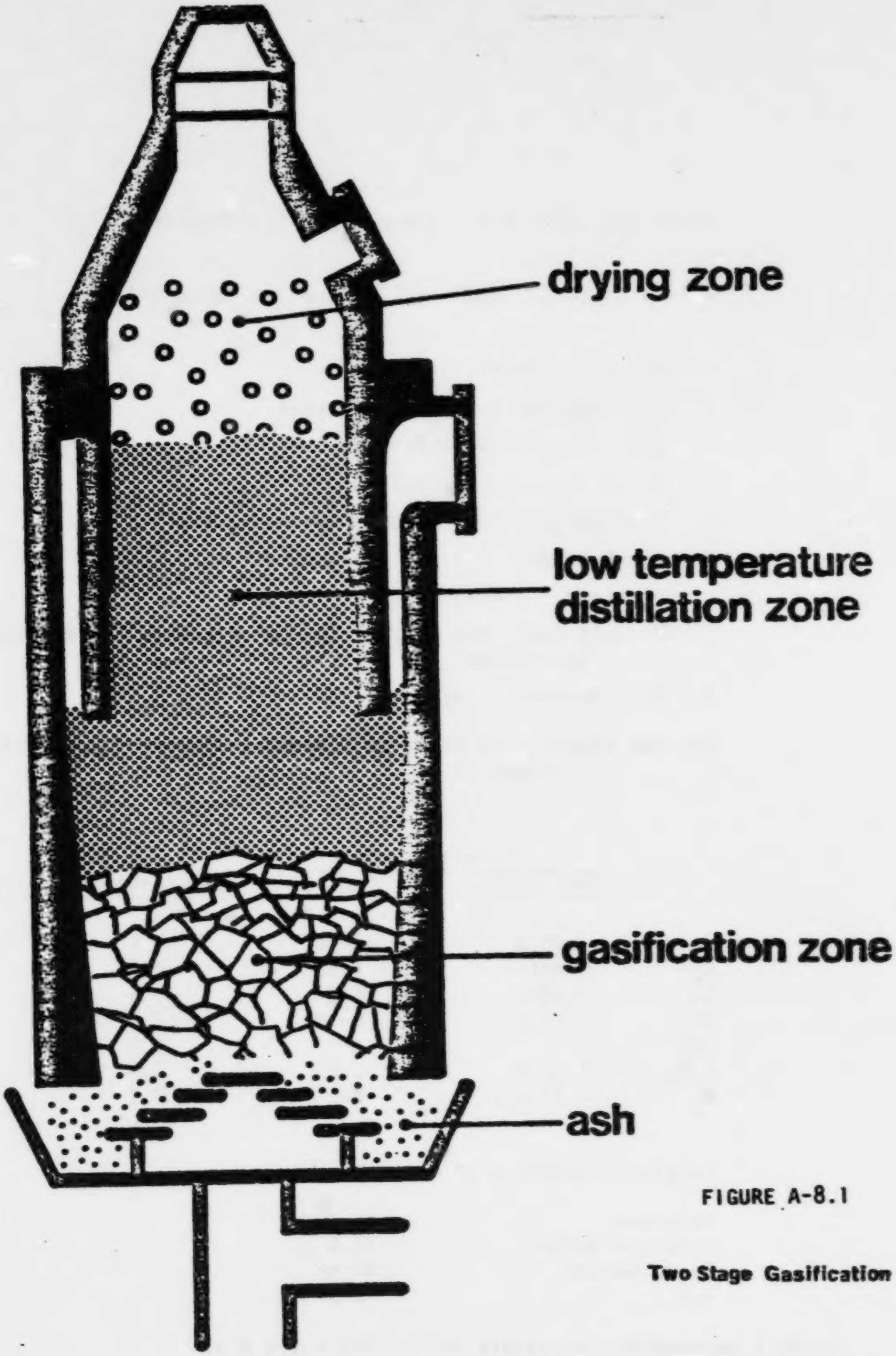

drying zone
low temperature distillation zone
gasification zone
ash

FIGURE A-8.1

**Two Stage Gasification**

Reference: Woodall-Duckham Brochure

TABLE A-8.1

## WD TWO-STAGE COAL GASIFICATION PLANTS

The WD Two-Stage process has been in commercial use as a cyclic medium-Btu gas generator since the 1920's and as a continuous air-blown fuel gas generator since 1942. Over 100 units have been built in Europe alone. The following lists are confined to plants built since 1946.

### A. Industrial Fuel Gas Plants

These units all employ a continuous air/steam blast as gasification agent. Different numbers of standard size gasifiers (there are several standard sizes) are used to obtain the required output. A variety of coal types are used, as indicated. Mixtures of different coals have also been successfully employed. Gas purification is included on some plants.

| Client and Location | Coal Type | No. of Units |
|---|---|---|
| Austrian-American Magnesia Co., Radenthein, Austria | Bituminous | 4 |
| VOEST Steelworks, Linz, Austria | Lignite/Bituminous | 3 |
| Cellulose & Paperworks, Frantschach, Austria | Lignite | 1 |
| Reforming Plant, Wels, Austria | Lignite | 1 |
| Gas Utility Co.,Graz, Austria | Lignite | 1 |
| Coke Plant, Strasbourg, France | Bituminous | 3 |
| Coke Plant, Drocourt, France | Bituminous/Coke | 3 |
| Steelworks, Audincourt, France | Bituminous | 1 |
| Steelworks, Firminy, France | Bituminous | 1 |
| English Steel Corp., Sheffield, England | Bituminous | 7 |
| Weldless Steel Tube Co., Wednesfield, England | Bituminous | 2 |

(Continued)

TABLE A-8.1 (Cont'd)

| Client and Location | Coal Type | No. of Units |
|---|---|---|
| Ziar Aluminum Works, Czechoslovakia | Bituminous | 7 |
| Chomutov Tube Works Czechoslovakia | Lignite | 14 |
| Istanbul Gas Utility Co., Turkey | Lignite | 1 |
| Australian Consolidate Industries Ltd., Sydney, Australia | Bituminous | 4 |
| Melbourne Gas Works Melbourne, Australia | Bituminous/Brown Coal | 2 |
| Elgin Fireclay Ltd., Springs, South Africa | Bituminous | 1 |
| Vaal Potteries Ltd., Meyerton, South Africa | Bituminous | 1 |
| Union Steel Corp., Johannesburg, South Africa | Bituminous | 2 |
| Stewards & Lloyds Steelworks South Africa | Bituminous | 3 |
| Masonite, Escault, South Africa | Bituminous | 3 |
| SAAPI, Mandini, South Africa | Bituminous | 2 |
| Rand Water Board, Vereeniging, South Africa | Bituminous | 1 |
| Driefontein, Carltonville, South Africa | Bituminous | 2 |
| Vereeniging Refractories South Africa | Bituminous | 2 |

(Continued)

TABLE A-8.1 (Cont'd)

## B. Public Utility Gas Plants

The following plants employ the same type of gasifiers, including coal and ash handling systems, as the Industrial Fuel Gas Plants, but operate in a cyclic mode so as to produce a gas with a very low nitrogen content. The calorific value of the product gas is from 330 to 500 Btu/cu. ft., depending on the extent of enrichment, e.g. by carburation with distillate or residual oil, or by enrichment with LPG.

| Location of Utility | No. of Units |
|---|---|
| St. Poelten, Austria | 2 |
| Naples, Italy | 2 |
| Rome, Italy | 5 |
| Trieste, Italy | 2 |
| Milan, Italy | 2 |
| LaSpezia, Italy | 1 |
| Como, Italy | 1 |
| Genoa, Italy | 4 |
| Vierzon, France | 2 |
| Dijon, France | 2 |
| Kensal Green, England | 1 |
| Gloucester, England | 1 |
| Ulm, West Germany | 2 |
| Freiburg, West Germany | 2 |
| Zagabria, Yogoslavia | 1 |
| Prague, Czechoslovakia | 6 |
| Warsaw, Poland | 3 |
| Thom, Poland | 2 |
| Tokyo, Japan | 5 |
| Posen, Poland | 3 |

(Continued)

TABLE A-8.1 (Cont'd)

## C. Synthesis Gas and Water Gas Plants

The manufacture of ammonia or methanol requires a low level of methane in the synthesis gas. Synthesis gas from coal is produced in WD plants by cyclic operation, including autothermic reforming of hydrocarbons, or by continuous gasification with oxygen or an oxygen/air mixture. If coke is specified as the feed, the upper (distillation) section of the gasifier is omitted.

| Client and Location | Mode | No. of Units |
|---|---|---|
| OSW Fertilizer Plant<br>Linz, Austria | Oxygen Blown | 4 |
| Vetrocoke, Porto Marghera,<br>Italy | Bituminous Coal,<br>Cyclic | 2 |
| Montecatini, Crotone, Italy | Oxygen Blown | 2 |
| Montecatini, St. Giuseppe<br>di Cairo, Italy | Oxygen Blown | 2 |
| I.M.A.D., Naples, Italy | Bituminous Coal,<br>Cyclic | 2 |
| State Works, Semtin,<br>Czechoslovakia | Coke, Cyclic | 4 |
| D. Swarovski Co.,<br>Wattens, Austria | Coke, Cyclic | 2 |
| Edison S.p.A., Milan, Italy | Coke, Cyclic | 1 |
| Marconi S.p.A., Aquila, Italy | Coke, Cyclic | 1 |
| Public Utility, Paris, France | Coke, Cyclic | 3 |
| Public Utility,<br>Fuerth, West Germany | Coke, Cyclic | 1 |

## SECTION B - DESCRIPTION OF GAS CLEAN-UP SYSTEMS ON OPERATING GASIFIER INSTALLATIONS

1. Introduction
2. Koppers-Totzek
3. Lurgi
4. Wilputte
5. Woodall-Duckham/Gas Integrale

## B.1 Introduction

Particulates, sulfur and nitrogen are the three pollutants in industrial gases that have received the most attention due to their potential environmental and health effects. Their removal has been standard practice for decades in the manufactured and natural gas industry. Perhaps more attention has been paid to the removal of particulates and sulfur than to nitrogen. It is only recently that health effects of nitrogen oxides have begun to be given serious consideration. Much of the need to remove particulates is associated with potential problems in compressing and/or burning dirty gases.

Raw coal-derived gases also contain tars along with sulfur compounds, and good removal of tars and particulates was a practical necessity in the early days of manufacturing and distributing coal-derived fuel gases. Hence, many years ago, means were developed to remove tars and particulates from raw gas streams. These methods may not be sophisticated in today's world but they served the purpose in their day. Many of these methods were dual-purpose schemes. For example, the dry box hydrated iron-oxide process removes essentially all hydrogen sulfide from the gas stream and will also remove traces of tar. Furthermore, in the event of an upset in the tar scrubbing system, the boxes will capture a slug of material. Although not specifically intended as such, the iron-oxide boxes were effective in preventing tars from entering the gas distribution system.

Because the industrial gas is burned in vented equipment (as compared to household gas which is frequently burned in nonvented equipment), the pollutant levels in industrial fuel can be somewhat higher than permitted in pipeline gas. It would appear reasonable to assume that industrial fuel gas should have about the same, or perhaps, as previously suggested, lower levels of contaminants as any alternative liquid fuel would have that complies with the Clean Air Act of 1971. Consequently, a basis can be established to evaluate and develop pollution control systems for the generation and use of industrial fuel gas from coal.

If a sulfur emission criterion of 0.5 lbs of $SO_2$ per $10^6$ Btu is used as a guide, application of this specification to a typical air-blown gasifier product shows that the degree of sulfur removal required for industrial fuel gas is substantially different from that required for pipeline gas. This difference can be clearly seen in Figure B-1.1 which has been prepared to show, in a generalized way, the effect of coal sulfur content on the degree of sulfur removal required to meet the proposed level. The chart has been based on calculations for a low heating value feed (lignite), a typical bituminous coal with a heating value of 12,500 Btu/lb, and the following assumptions:

a. 75% gasification efficiency
b. 80% of the sulfur in the coal appears in the raw product gas.

For other coals, a generalized formula for sulfur removal is given in the Appendix. The sulfur removal curve for pipeline gas looks as if it were a vertical straight line because all the values are so close to 100%, but some of the points as calculated follow:

K+E 10 X 10 TO THE CENTIMETER 18 X 25 CM.
KEUFFEL & ESSER CO. MADE IN U.S.A.
46 1510

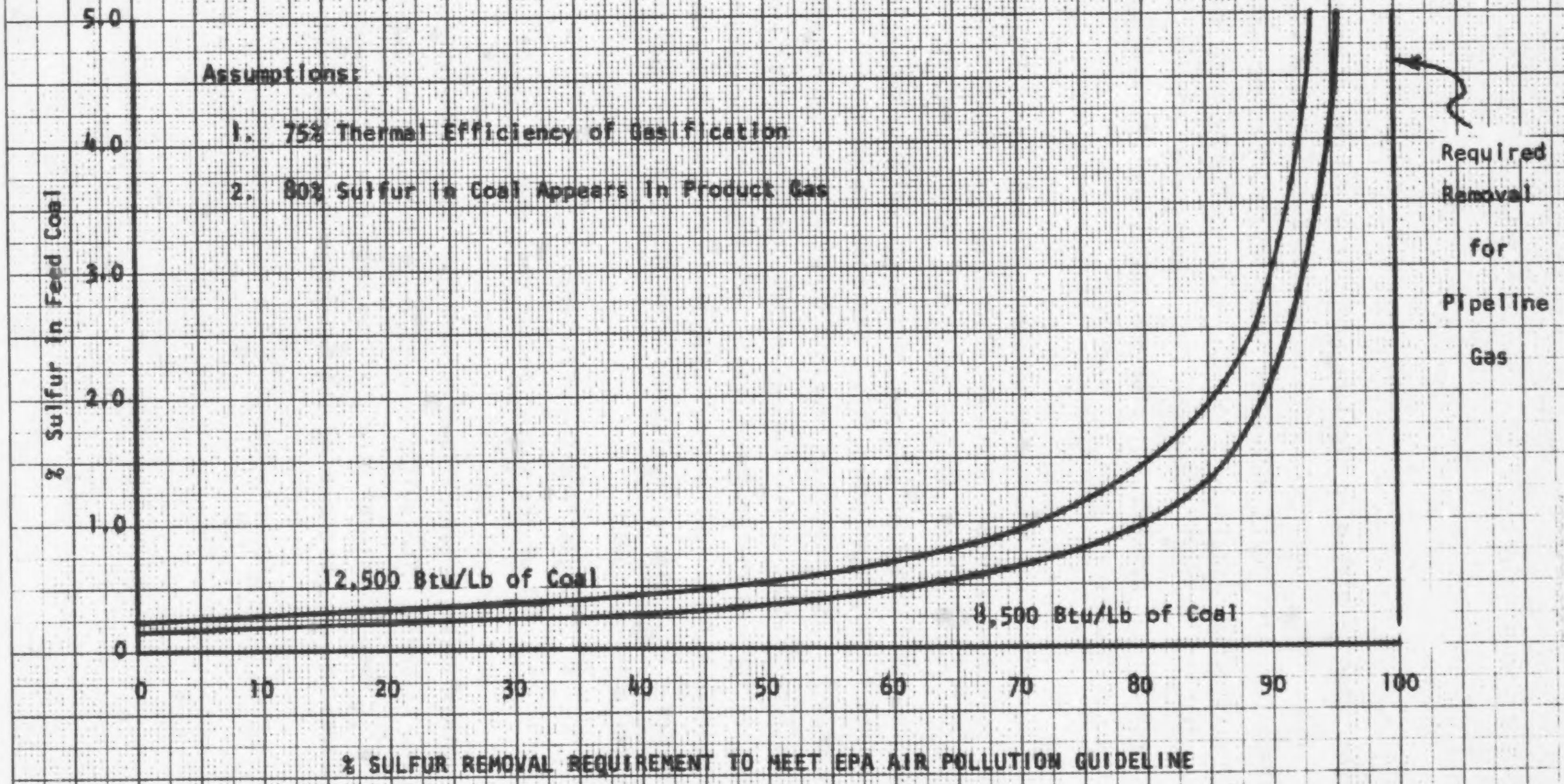


FIGURE B-1.1 SULFUR REMOVAL REQUIREMENT FOR INDUSTRIAL FUEL

| % Sulfur in Coal | % Removal for Pipeline Gas |
|---|---|
| 0.2 | 99.79 |
| 0.5 | 99.92 |
| 1.0 | 99.96 |
| 2.0 | 99.98 |
| 5.0 | 99.99 |
| 10.0 | 99.996 |

While pipeline gas requires just about complete sulfur removal, the chart shows that a 1.45% sulfur coal with a 12,500 Btu/lb heating value would require only 80% removal from the raw product gas to meet the 0.5 lb $SO_2$ per $10^6$ Btu level. Even when processing coals of a high sulfur content, there is a great difference in the required removal efficiency for the two gases. These generalized curves are of importance because they show the great difference in sulfur removal requirements to prepare an industrial fuel as compared to pipeline gas. This difference manifests itself in sulfur removal process selection and the design criteria for these processes.

The technology of the past two decades has been developed and improved from the point of view of essentially total sulfur removal from gases as would be required for the pipeline industry and the chemical industry. This currently practiced technology of almost total sulfur removal is examined in this section in consideration of its proven capability, but a new look at partial removal of sulfur is recommended. The ability to achieve a level of removal exceeding industrial fuel requirements suggests that partial removal might be easier and more economical.

## B.2 Clean-up System for the Koppers-Totzek Gasifier

### Gasification:

The Koppers-Totzek gasifier and a proposed clean-up system for producing clean, desulfurized utility gas or synthesis gas is shown schematically in Figures B-2.1 and B-2.2. Oxygen, steam and coal react in the gasifier, converting the coal volatile matter and carbon into gas and the coal ash into molten slag. About 50 to 70% of this slag leaves the gasifier through the bottom and solidifies upon contact with water in the quench tank situated beneath the gasifier. The remainder of the slag, along with any ungasified carbon, is entrained with the gas leaving the top of the gasifier. If necessary, water sprays freeze any slag droplets prior to entry into the waste heat boiler to prevent solidification on the tubes. In the waste heat boiler, steam up to 1500 psig is generated.

A typical composition for the gasifier outlet gas before any clean-up is given in Table B-2.1. As shown, the gas may have about 12 grains/SCF of particulates, 0.2-0.3% $H_2S$ and COS, and about 0.2% nitrogen compounds including ammonia, cyanides and oxides of nitrogen. Due to the high reaction temperature, phenols, pyridenes, tar, oil or other condensable hydrocarbons are not contained in the gas.

FIGURE B-2.1

## KOPPERS-TOTZEK PROCESS
## GASIFICATION, COOLING & PARTICULATE REMOVAL

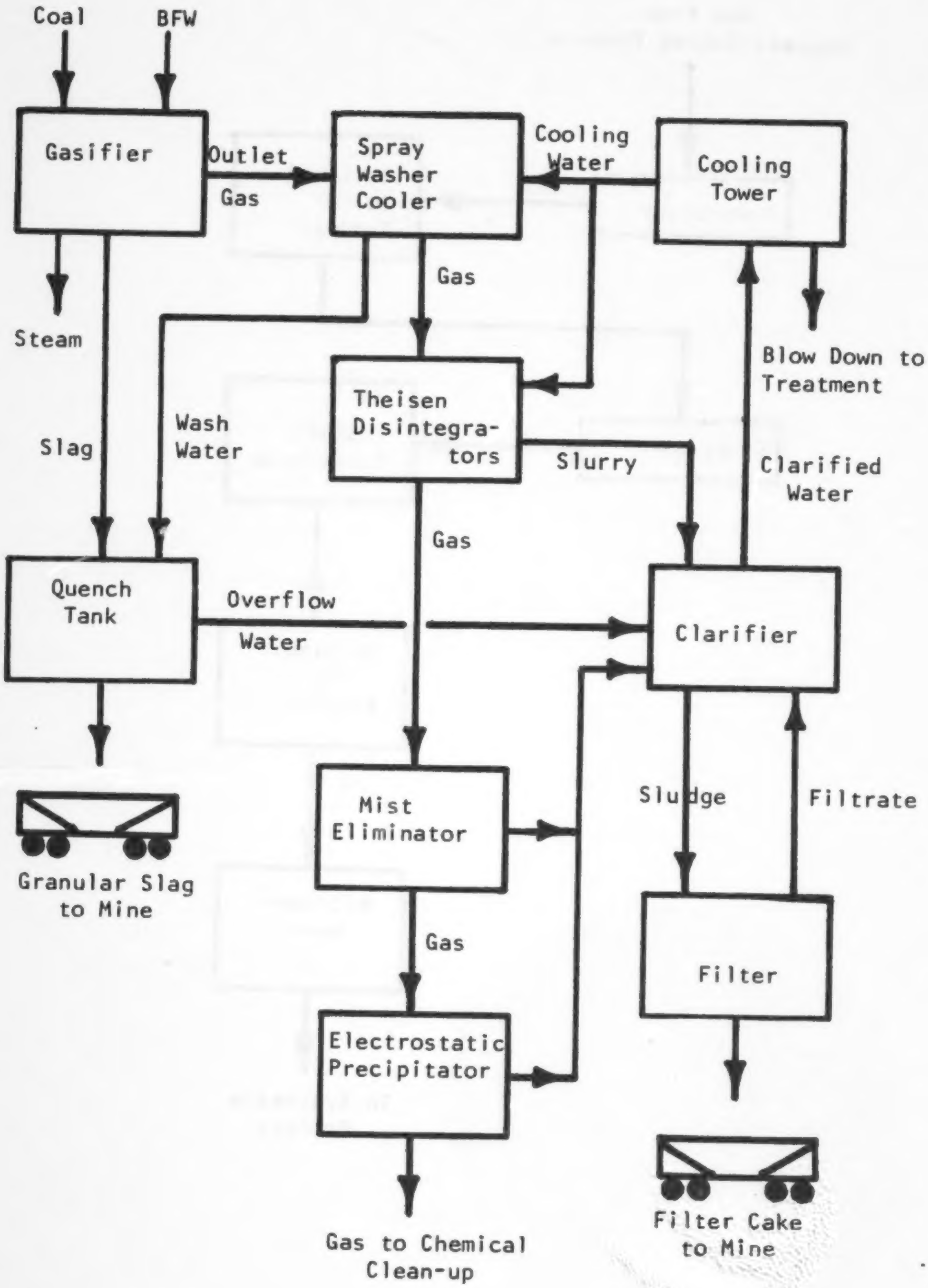
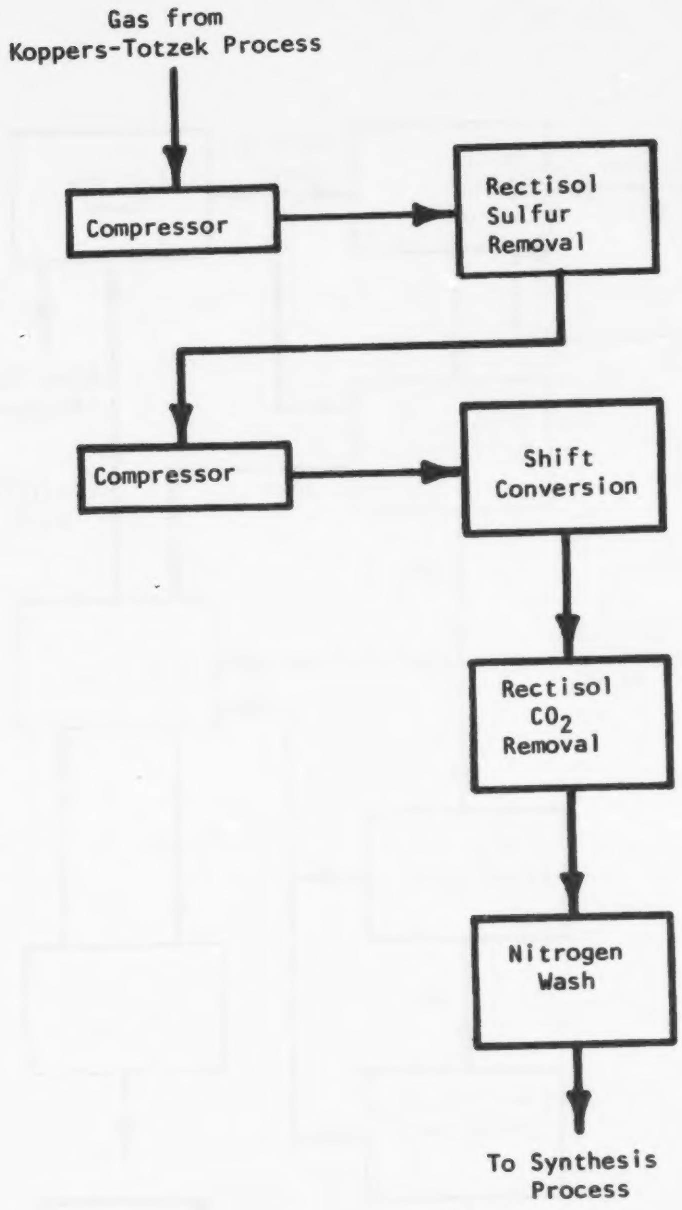

Coal
BFW
Gasifier
Outlet Gas
Spray Washer Cooler
Cooling Water
Cooling Tower
Steam
Gas
Blow Down to Treatment
Theisen Disintegrators
Wash Water
Slag
Slurry
Clarified Water
Gas
Quench Tank
Overflow Water
Clarifier
Sludge
Filtrate
Mist Eliminator
Granular Slag to Mine
Gas
Filter
Electrostatic Precipitator
Filter Cake to Mine
Gas to Chemical Clean-up

FIGURE B-2.2

GAS PREPARATION FOR SYNTHESIS


Gas from
Koppers-Totzek Process
Compressor
Rectisol
Sulfur
Removal
Compressor
Shift
Conversion
Rectisol
$CO_2$
Removal
Nitrogen
Wash
To Synthesis
Process

## TABLE B-2.1

## KOPPERS-TOTZEK GASIFIER GAS COMPOSITIONS

(Coal Unspecified)

| | Volume Percent | |
|---|---|---|
| Component | Gasifier Outlet | To Compression & Acid Gas Removal |
| CO | 37.36 | 49.50 |
| $CO_2$ | 7.13 | 9.42 |
| $CH_4$ | 0.08 | 0.11 |
| $H_2$ | 25.17 | 33.35 |
| $N_2$ | 0.30 (1) | 0.40 |
| $H_2S$ | 0.23 | 0.30 |
| COS | 178 ppmv | 235 ppmv |
| HCN | 288 ppmv | 300 ppmv |
| $NH_3$ | 0.17 | 0.22 |
| $H_2O$ | 29.19 | 6.20 |
| Ar | 0.32 | 0.42 |
| $SO_2$ | 22 ppmv | 15 ppmv |
| NO | 7 ppmv | 7 ppmv |
| Particulates (grs/SCF) | 11.57 | <0.002 |

NOTE: (1) Possible Sources of Nitrogen With Oxygen-Blown Gasification includes Impurity in Feed Oxygen and Conversion of Fuel-Bound Nitrogen

Reference: Farnsworth, J.F., Mitsak, D.M., Kamody, J.F., "Clean Environment with K-T Process", presented at EPA Meeting: Environmental Aspects of Fuel Conversion Technology, May, 1974.

### Gas Cooling with Particulate Removal:

The next two or three process steps reduce the particulates in the gas to very low levels. The effluent stream from the waste heat boiler enters a washer-cooler where sprays of water cool the gas from 350°F to about 100°F while simultaneously removing 90% of the entrained particles. Then two Theisen-type irrigated disintegrators in series reduce the dust loading to about 0.002 grains per SCF. If the gas is to be compressed to high pressures for chemical synthesis or for the production of high Btu gas, wet-type electrostatic precipitators are used to reduce particulates to 0.0001 grains per SCF. For compression up to 175 psi, precipitators may not be necessary and the gas, after passing through a mist eliminator and fan, would be manifolded into the suction of the gas compressors. The composition of the gas at this point may also be seen in Table B-2.1.

When Koppers (U.S.A.) first undertook design of Koppers-Totzek gasification units, they introduced the venturi scrubbers as a substitute for the washer-cooler and Theisen disintegrator system. Since no units had been built that way, the German Koppers Company took a conservative position and suggested a return to the original design proposal. While the venturi system does consume power, use of the disintegrator units requires even more power consumption. Each of the two Theisen units would require 700 HP for gas from one 4-headed or two 2-headed gasifiers. With the venturi system, the gasifier is operated at slightly increased pressure to provide the 50 inches of water pressure loss in the venturi scrubbers. The first unit that might be installed in the U.S.A. is likely to have Theisen units because the designers will look favorably on the proven approach. However, in the future, venturi scrubbers might be a good alternate choice. For blast furnace applications, venturi scrubbers are now being installed rather than Theisen disintegrators.

Cooling Water Clean-up:

Particulate-laden waters from gas cleaning and cooling plus overflow from the quench tank are piped to a clarifier. Thickened clarifier sludge is filtered, and the filtrate is returned to the clarifier. Filter cake and granular solids removed from the quench tank by means of a scraper-conveyor assembly are loaded into railroad cars for disposal at the mine site. Clarified water is pumped to a cooling tower and recirculated to the gas cooling/cleaning and the solids quench systems.

Water recirculation permits the build-up of many chemicals in the water. Analyses at various steps in the process have been reported from a plant in Kutahya, Turkey. The data given in Table B-2.2 show the order of magnitude of the chemical concentrations and identify some possible contaminants. Although not reported in the Kutahya washer-cooler analysis, dissolved $H_2S$ might be expected and therefore stripped out by air in the cooling tower. If all the dissolved $H_2S$ were stripped into the air, the discharge air concentration would be 1-2 ppm by volume. While this is far above the odor threshold, Koppers Company experience shows that there is no odor problem. A previous Environmental Protection Agency study verifies this finding (K-T Reference #6). Appreciable bioxidation, common in the cooling water circuit, may account for the indicated analytical results and Koppers' observations.

TABLE B-2.2

## KOPPERS COAL GASIFICATION

## WATER ANALYSES, KUTAHYA, TURKEY(1)

| Sample Location | | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| pH Value | | 8.8 | 8.8 | 8.9 | 7.5 | 8.8 | 8.9 | 8.9 |
| Conductivity | mho/cm | 7.6<br>$10^{-4}$ | 1.8<br>$10^{-3}$ | 2.0<br>$10^{-3}$ | 9.7<br>$10^{-4}$ | 1.8<br>$10^{-3}$ | 1.8<br>$10^{-3}$ | 1.7<br>$10^{-3}$ |
| Total Hardness | ° dH | 20.8 | 33.5 | 36.8 | 22.8 | 34.0 | 34.8 | 35.2 |
| CaO | mg/l | 78 | 101 | 78 | 85 | 135 | 179 | 179 |
| MgO | mg/l | 97 | 161 | 194 | 102 | 145 | 113 | 129 |
| Ma | mg/l | 17.5 | 17.5 | 17.5 | 17.5 | 17.5 | 17.5 | 17.5 |
| K | mg/l | 5.6 | 8.8 | 10.0 | 6.8 | 8.0 | 8.0 | 7.9 |
| Zn | mg/l | 0.01 | 0.03 | 0.02 | 0.03 | 0.02 | 0.02 | 0.02 |
| Fe | mg/l | 0.05 | 0.22 | 1.95 | 0.26 | 0.20 | 0.64 | 0.24 |
| $NH_4$ | mg/l | 0.32 | 157 | 184 | 25 | 137 | 122 | 72 |
| $NO_2$ | mg/l | 0.02 | 0.13 | 4.47 | 5.34 | 0.24 | 4.37 | 23.7 |
| $NO_3$ | mg/l | 58.2 | 3.32 | 13.7 | 34.0 | 24.7 | 22.9 | 42.0 |
| $PO_4$ Total | mg/l | 1.89 | 0.81 | 1.21 | 1.69 | 0.81 | 2.70 | 2.41 |
| Cl | mg/l | 18 | 85 | 96 | 53 | 57 | 46 | 36 |
| $SO_4$ | mg/l | 42 | 216 | 155 | 147 | 255 | 109 | 153 |
| CN | mg/l | 0.26 | 0.52 | 12.5 | 7.0 | 1.4 | 14.0 | 0.7 |
| $H_2S$ | mg/l | ---------------------Not Detected--------------------- | | | | | | |
| $KMnO_4$ Consumed | mg/l | 8 | 9 | 400 | 14 | 11 | 145 | |
| COD | $mgO_2/l$ | 14 | 18 | 128 | 18 | 16 | 63 | 60 |
| $SiO_2$ | mg/l | 14.8 | 16.0 | 14.8 | 30.6 | 19.8 | 42.6 | 30.6 |
| Suspended Solids | mg/l | 14 | 4612 | 5084 | 278 | 3072 | 50 | 58 |
| Hot Residue, 800°C | mg/l | 4 | 3918 | 4356 | 134 | 2690 | 46 | 42 |
| Stripped Residue | mg/l | 568 | 812 | 940 | 606 | 706 | 724 | 828 |
| Hot Residue, 800°C | mg/l | 268 | 550 | 588 | 366 | 526 | 512 | 534 |
| Cu | mg/l | 0.01 | 0.01 | 0.01 | 0.06 | 0.01 | 0.06 | 0.27 |

1) Cooling water to gasifier seal pot.

2) Water from the gasifier seal pot.

3) Wash water after washer-cooler.

4) Wash water after Theisen washer.

5) Water into clarifier.

6) Water out of clarifier.

7) Water out of cooling tower.

NOTE: 1) Process Water Streams Circulated within Process Unit. Any purge Stream from the System Would Require Treatment before Discharge.

Reference: Farnsworth, J.F., Mitsak, D.M., Kamody, J.F., "Clean Environment with K-T Process", presented at EPA Meeting: Environmental Aspects of Fuel Conversion Technology, May, 1974.

An additional cooling tower effluent is the drift loss of mist from the cooling tower. The mist will contain dissolved and suspended solids, which will result in deposits on the ground and on nearby equipment. To minimize solids build-up in the cooling tower circulation and the intensity of its attendant problems, blowdown is necessary. Acceptable stream standards must be met by treatment of the blowdown, principally to destroy HCN and $NH_3$ through chemical chlorine oxidation and pH adjustment. Evaporation, windage and blowdown water losses at the cooling tower, plus moisture in the filter cake from clarifier sludge and in slag, necessitate the addition of a small quantity of make-up water to this system. If water is at a premium, air cooling may be used for cooling down to 140°F in certain applications and the cooling tower can be reduced in size to provide only the final trim in water temperature.

### Gas Clean-up:

The cool, clean gas leaving the gas cleaning system contains sulfur compounds which must be removed to meet gas specifications. The type of system chosen depends upon the end uses and pressure of the product gas. For low pressures (up to 150 psig) and low Btu gas application, there are the chemical reaction processes, such as amine and carbonate systems. At higher pressures, the physical absorption processes, such as Rectisol, Purisol and Selexol, are recommended. The choice of the process is also dependent upon the desired purity of the product gas and the desired selectivity with respect to the concentrations of carbon dioxide and sulfides.

There are several acid gas removal processes with the capability of reducing the sulfur content in the gas to 5 ppm by volume. The processes are based on absorption in solution and subsequent stripping of the acid gases, $H_2S$ and $CO_2$, from the solution. The physical absorption processes, which operate at pressures of 300-400 psig, exhibit the greatest selectivity with respect to hydrogen sulfide and carbon dioxide removal. Since no chemical reactions occur, these processes do not form stable compounds, such as thiosulfates and thiocyanates. Some chemical reaction processes, such as carbonate and amine, which form the aforementioned stable compounds, can be used but will require periodic dumping of the solution in order to maintain removal efficiency. Dumped solution will require treatment to meet permissible discharge limitations. The choice of process is dependent upon economics, environmental control, purity of product gas, and desired acid gas selectivity. A plant can be designed to reduce sulfur in product gas to 5 ppm by volume, control the $H_2S$ level in carbon dioxide to 10 ppm by volume, and control the liquid effluent to zero pollutants.

The Koppers Company, it is understood, is proposing the use of MDEA (methyl diethanolamine) for selective removal of $H_2S$. This chemical has sufficient selectivity to provide about a 22% $H_2S$ concentration in the acid gas to the Claus plant. The acid gas removal facilities consist of a COS hydrolysis column followed by an absorber. Within the COS hydrolysis column, the gas is contacted with hot circulating MDEA solution to promote hydrolysis of COS to $H_2S$ in order to facilitate a high degree of sulfur removal within the absorber. The acid gases are stripped from the MDEA absorbent and sent to Claus units. Gas leaving each $H_2S$ absorber contains approximately 115 ppm of $H_2S$, plus COS, or 0.076 pounds of $SO_2$ equivalent per million Btu of gross heat content of the fuel gas.

At the African Explosives and Chemical Industries Ltd. ammonia plant in South Africa, where coal is gasified using the Koppers-Totzek process, gas is cleaned up with the Rectisol process. First a methanol wash at -36°F and 30 atm. desulfurizes the gas. Then carbon dioxide is removed, following the CO shift conversion, by washing with methanol at -72°F and 51 atm. Finally, residual CO, argon and methane are removed by washing with liquid nitrogen at -310°F (K-T Reference #10).

The acid gas stream, containing a minimum of 14 volume percent $H_2S$, is catalytically converted to elemental molten sulfur in a Claus unit. The tail gases exiting the Claus unit contain $SO_2$ and can be treated to catalytically reduce the $SO_2$ to $H_2S$. Scrubbing with an amine solution absorbs the $H_2S$, and subsequent stripping yields an $H_2S$ stream which is recycled to the Claus unit. This combination results in overall sulfur recovery of 99+%.

## B.3 Clean-up System for the Lurgi Gasifier

Gasification:

The Lurgi gasifier and its clean-up system for producing SNG has been carefully studied and, therefore, is illustrated in Figures B-3.1, B-3.2 and B-3.3 The proposed El Paso Burnham Coal Gasification Complex exemplifies such an application for the Lurgi process when used for pipeline gas. Industrial gas, as explained in the Introduction, would require less stringent control of pollutants and thus, would provide more flexibility in the control methods for pollutants.

Coal entering from lock hoppers reacts with a mixture of oxygen and process steam introduced into the bottom of the gasifier. About 86% of the coal fed to the gasifier is gasified and the remaining 14%, which is mostly carbon, is burned in the combustion zone. Ash, bearing only a very small amount of unburned carbon, passes down through the grate, out of the gasifier through an ash lock hopper, and into an ash bin where ash is cooled by water quenching. The ash is separated from quench water in a clarifier and sent to the mine site for disposal. It is estimated that 1.4% of the DAF coal is not consumed and leaves with the ash.

Gas Quenching:

Raw gas leaves the gasifier at about 850°F containing carbonization products such as tar, oil, naphtha, phenols, ammonia, and traces of coal and ash dust. On an oil-free and dry-gas basis, the gas leaving the gasifier will have the following approximate composition:

FIGURE B-3.1

## LURGI PROCESS
## GASIFICATION AND ASH HANDLING

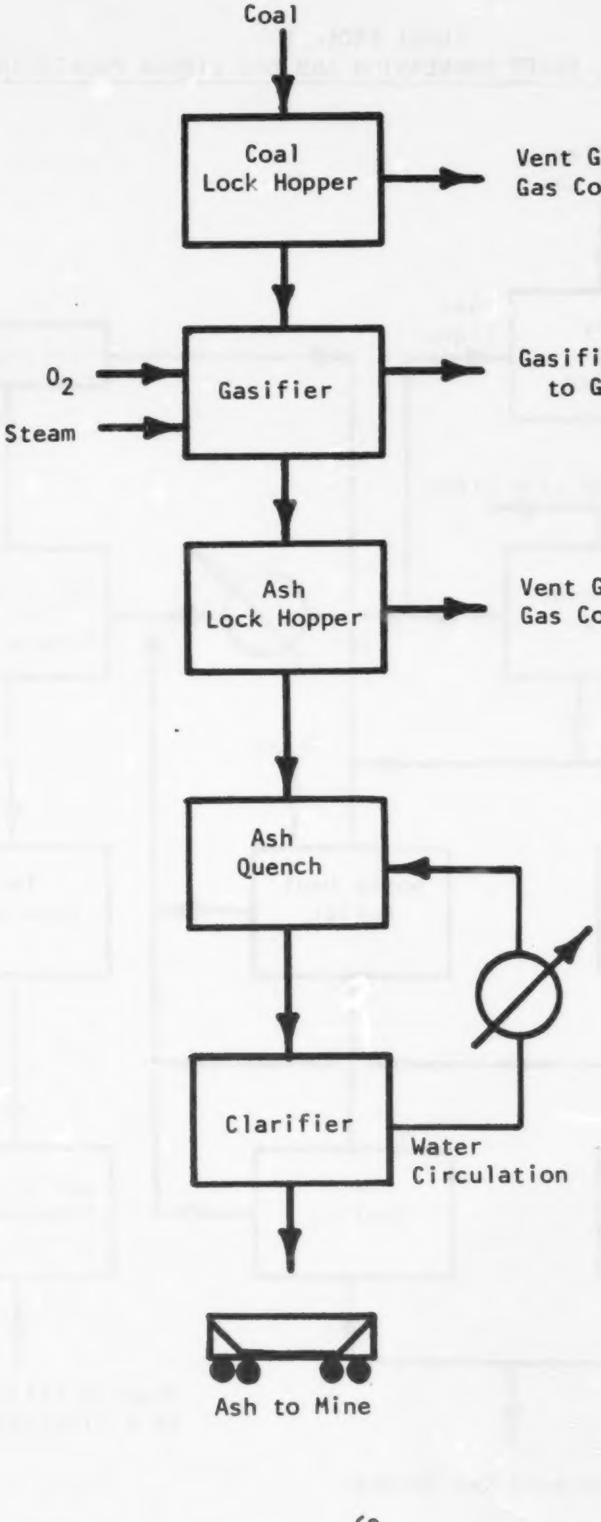

Coal
Coal Lock Hopper
Vent Gas to Gas Cooling
$O_2$
Steam
Gasifier
Gasifier Outlet Gas to Gas Cooling
Ash Lock Hopper
Vent Gas to Gas Cooling
Ash Quench
Clarifier
Water Circulation
Ash to Mine

FIGURE B-3.2

## LURGI PROCESS
## GAS COOLING, SHIFT CONVERSION AND GAS LIQUOR PROCESSING

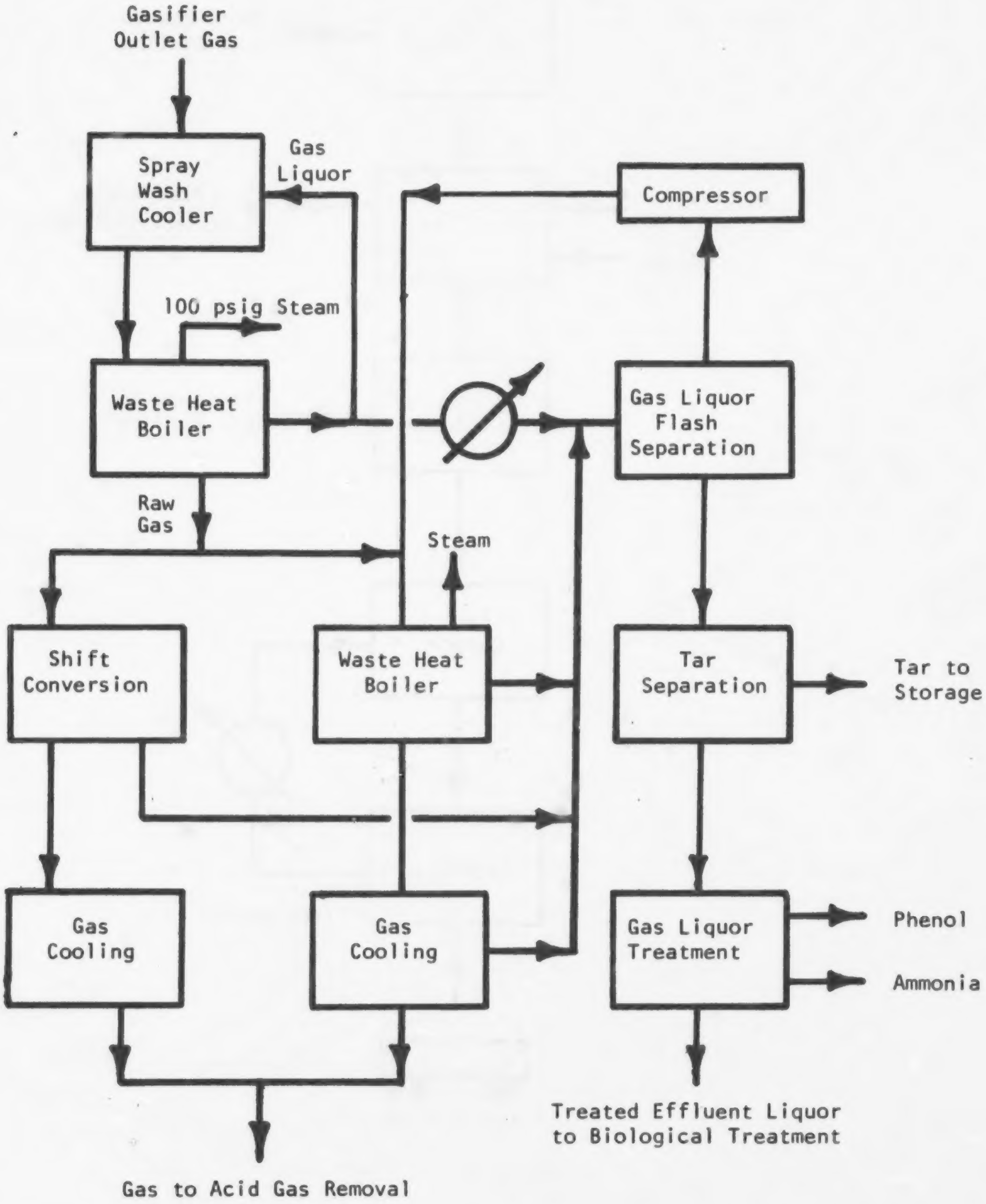
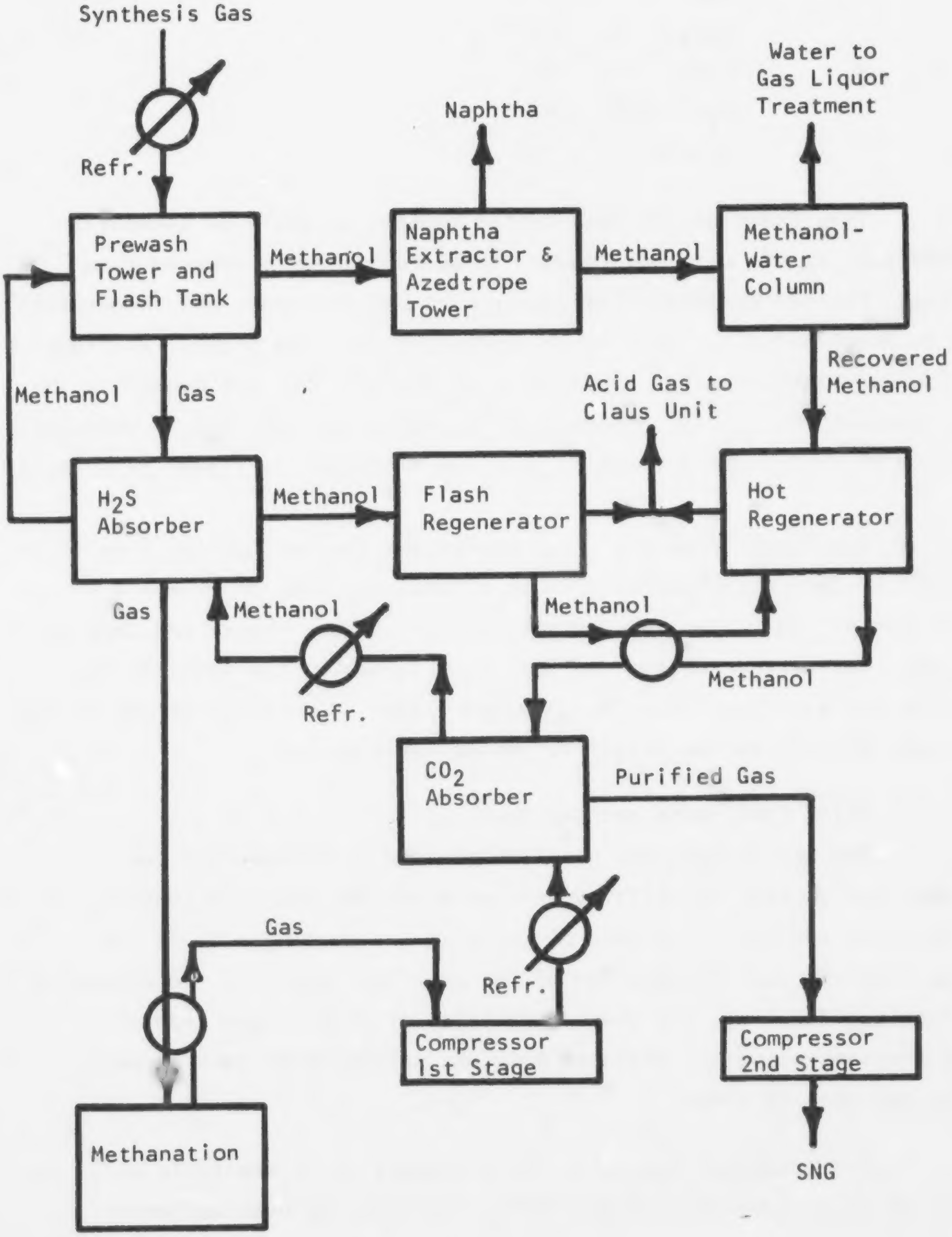

Gasifier Outlet Gas
Spray Wash Cooler
Gas Liquor
Compressor
100 psig Steam
Waste Heat Boiler
Gas Liquor Flash Separation
Raw Gas
Steam
Shift Conversion
Waste Heat Boiler
Tar Separation
Tar to Storage
Gas Cooling
Gas Cooling
Gas Liquor Treatment
Phenol
Ammonia
Treated Effluent Liquor to Biological Treatment
Gas to Acid Gas Removal

FIGURE B-3.3

RECTISOL GAS CLEAN-UP AND METHANATION


Synthesis Gas
Refr.
Naphtha
Water to Gas Liquor Treatment
Prewash Tower and Flash Tank
Methanol
Naphtha Extractor & Azedtrope Tower
Methanol
Methanol-Water Column
Recovered Methanol
Methanol
Gas
Acid Gas to Claus Unit
H₂S Absorber
Methanol
Flash Regenerator
Hot Regenerator
Gas
Methanol
Methanol
Refr.
Methanol
CO₂ Absorber
Purified Gas
Gas
Refr.
Compressor 1st Stage
Compressor 2nd Stage
SNG
Methanation

| | |
|---|---|
| $CO_2$ | 28.6 Mol% |
| CO | 20.2 |
| $H_2$ | 37.9 |
| $Ch_4$ | 11.4 |
| $C_2H_4$ | .42 |
| $C_2H_6$ | .62 |
| $H_2S$ + COS | .49 |
| $N_2$ + A | .33 |

This crude gas is then cooled rapidly to 400°F by quenching in the spray washer with gas liquor, an aqueous phase condensed from the gas. Further cooling in the waste heat boilers drops the temperature down to about 360°F to 370°F while generating 100 psig steam. As higher boiling tar fractions are condensed, coal and ash dust are bonded to the tar. Some of the liquid condensed in the waste heat boilers is recycled to the wash coolers, and the excess is drawn off to gas liquor separation.

Gas liquor from the spray washer and the gas cooling area is flashed to atmospheric pressure in an expansion vessel to remove dissolved gases. Heavy tar is separated out in another vessel and sent to storage. The mixture of tar and dust is returned to the gasifier for cracking and gasification. The detarred liquor is sent to the gas liquor treatment area to remove dissolved phenol and ammonia.

Shift Conversion and Gas Cooling:

Raw gas leaving the gasifier section is divided into two streams; one is sent to shift conversion where the hydrogen content is increased and the other goes directly to gas cooling. Crude gas vented from the cyclic operation of the coal lock hoppers, the expansion gas from gasification, and small quantities of recycle gas from other areas are compressed and injected into the stream which goes directly to the gas cooling area.

The crude gas bypassing shift conversion is cooled in a series of units comprised of the following: a waste heat boiler generating 60 psig steam, a low pressure steam generator, an air cooler and possibly a water trim cooler. Gas liquor and tar from the first two units are transferred to the primary gas liquor separator. The remaining condensate streams, comprised of gas liquor and a tar oil naphtha mixture, are separated in a second gas liquor separator.

Converted gas is cooled by the following series: exchange with boiler feedwater, generating low pressure steam, boiler feedwater deaeration, and finally air and water trim cooling. The two gas streams are combined into a single stream before acid gas removal. Gas liquor and condensate from the first three steps are cooled and combined with condensate streams from subsequent cooling. The total stream is then sent to the gas liquor separator where separation of the tar oil naphtha mixture from gas liquor will occur. Gas liquor will be pumped to the gas liquor treatment area and the tar oil mixture will be transported to storage.

Gas Liquor Treatment:

Gas liquor condensed in coal gasification and gas processing contains phenols, ammonia, carbon dioxide, hydrogen sulfide and caustic effluent. The Lurgi Phenosolvan Process can be used to recover the phenols. Ammonia is recovered in aqueous solution. The other contaminants are removed from the liquor by heating and stripping.

Incoming gas liquor entering the Phenosolvan Process is filtered in gravel filters to remove suspended matter. The filtered liquor is then mixed with an organic solvent (isopropyl ether) in the extractors where phenols are dissolved in the solvent. The phenol-rich solvent extract is collected for feed to the solvent distillation column, where crude phenol is recovered as the bottoms product and solvent as the overhead product. Recovered solvent is separated from the water by settling and then, with some make up of fresh solvent, recycled to the extractors.

Before being heated and steam stripped, the lean liquor (raffinate) from the extractors is stripped with fuel gas to remove traces of solvent which are picked up in the extraction step. The resulting solvent-laden fuel gas is scrubbed with crude phenol to recover the solvent. The phenol-solvent mixture is then fractionated in the solvent recovery stripper to produce the crude phenol product and collect the solvent for recycle to the extraction step.

Solvent-free liquor is heated and steam stripped to remove carbon dioxide, hydrogen sulfide and ammonia. The carbon dioxide and hydrogen sulfide are removed separately from the ammonia and returned to the process for sulfur recovery.

Ammonia is stripped from the liquor and condensed as an aqueous solution of about 25 weight percent $NH_3$. In the event that a market does not develop for this product, the wet ammonia vapor can be consumed as plant fuel provided $NO_x$ emissions are within limits.

Treated effluent liquor from the ammonia stripper is cooled and delivered to the biological treatment plant for further reduction of contaminants to render it suitable for use as cooling tower make-up. Before biological treatment, the effluent contains less than 20 ppm phenols and less than 60 ppm free ammonia. Afterward, the effluent meets the regulations for disposal of waste liquor.

Gas Clean-up and Methanation:

For SNG manufacture, the gas purification plant is designed to remove $H_2S$ and COS to a total sulfur concentration of 0.1 ppm by volume using the Lurgi Rectisol Process. After methanation and first-stage compression, the gas is washed to reduce $CO_2$ content. Because of the low operating temperatures (down to -50°F), all hydrocarbons heavier than $C_2$ are removed, leaving a very clean gas stream for the methanation section.

The mixed gas is chilled before entering the prewash tower where water and naphtha are removed by cold methanol wash. Naphtha is recovered from methanol and water by means of the naphtha extractor. Naphtha recovery is maximized by recycling the naphtha-methanol mixture through the azeotrope column. The methanol is recovered by distillation in the methanol-water column.

The naphtha-free gas enters the $H_2S$ absorber where $H_2S$ and COS are removed down to 0.1 ppm by volume total sulfur by cold methanol wash first used for $CO_2$ absorption. Heat of absorption is removed by refrigeration. Some of the absorbed acid gases are removed from the methanol wash by multi-flash in the flash generator. The remaining acid gases are completely stripped in a second regenerator operating at a higher temperature. All the acid gas streams are combined and delivered to the sulfur recovery plant.

The sulfur-free synthesis gas leaves the Rectisol Unit absorber, exchanges heat with returning methanated gas to save on refrigeration, and moves on to the methanation unit. The returned methanated gas enters the $CO_2$ absorber. The $CO_2$ content of the gas is reduced by regenerated cold methanol wash. The heat of absorption is removed by a refrigerant. The high Btu purified dry gas is warmed and sent to the second-stage compression unit.

The mechanical compression refrigeration unit provides refrigeration at two temperature levels. The high temperature level refrigeration (32°F) is used to condense most of the water out of the mixed gas and the methanation product gas. The remaining water vapor in the gases is prevented from freezing by methanol injection. The low temperature level refrigeration (about -50°F) is used to achieve the low temperature required for effective methanol wash.

## B.4 Wilputte Gas Clean-up System

The Wilputte gasifier is a moving-bed gasifier, operating at atmospheric pressure. The operating principles are described in Wilputte Bulletin No. 7662. as quoted below:

> "The gasification process is counter current. Thus, the coal is fed downward and the gas flow is upward. Moist air flows upward through an ash zone to the cumbustion zone, in which the carbon residue from pyrolyzed coal is burned to carbon dioxide (the water in the air does not enter this reaction). Various reactions occur in the bottom of the coal bed which lays directly above the combustion zone. The carbon reacts with the carbon dioxide to form carbon monoxide or with water to form hydrogen and carbon monoxide or carbon dioxide. In the middle of the coal bed, carbon reacts with carbon dioxide to from carbon monoxide. In the top of the coal bed, coal is pyrolyzed to form a carbon residue and volatile hydrocarbon products. The coal in the top of the charge passes through a plastic state when it becomes heated to about 850°F if the coal is a coking coal. A rotating rabble arm is used to mix and break up this plastic layer so as to get a uniform distribution for the upward flow of gas."

An example of the gas clean-up system used on Wilputte gasifiers is the installation at the Holston Defense Corporation in Tennessee. This plant consists of 12 gasifiers each having a diameter of 9'-2". Each unit is rated at 24 T/D of coal feed. The plant was built in 1945. Two gasifiers at any one time are in operation using a metallurgical grade of bituminous coal having a sulfur content of less than 1%. These gasifiers have had an excellent maintenance record. The original brick lining in the gasifier is still in use.

A very simple and straightforward gas clean-up system is used on the Holston gasifier installation. Raw gas leaves the gasifier at a temperature of about 1100°F and enters a refractory lined cyclonic-type separator that removes larger sized entrained particles. The gas then flows to a "primary gas cooler" through a collector main. Hot liquor is sprayed into the main reducing the gas temperature to about 200°F and removing the bulk of the tar prior to entry into the cooler. No waste heat is recovered from the gasifier effluent stream.

The "primary gas cooler" is packed tower that is irrigated with cooled liquor. Condensed tars and wash liquor from the collector main and the gas cooler flow by gravity to a sump where separation of liquor and tar occurs. The tar has a specific gravity of about 1.15 and therefore settles to the bottom of the sump. This material is pumped to storage for subsequent use as a boiler fuel. Solids are periodically raked from the sump.

Liquor from the sump is pumped and recirculated in a split-flow arrangement. Part of the liquor is returned directly to the collector main as"hot" liquor while the remaining part is cooled via water exchange to enter the top of the cooler. Excess liquor is treated by sand filters and carbon absorption to produce an acceptable effluent stream.

Overhead has from the "primary gas cooler", which actually is a counter-current gas scrubber, flows to an exhauster that boosts the scrubbed gas to a fuel gas header pressure of about 10 psi. The gas then flows to the individual burners for combustion without a sulfur removal step.

As can be seen, the clean-up system is extremely simple, comprising no moving parts other than the tar and liquor pumps and the exhauster. Over 30 years of operation of this gas clean-up system is ample proof of its basic operability and simplicity. Unfortunately, this simplicity cannot be maintained if the plant were to operate on a high-sulfur coal and would, therefore, require sulfur clean-up on the gas product. Nevertheless, the existing gas clean-up system used at the Holston installation is a working example of a simple, pratical approach to removing tar, dust and some ammonia from a coal gasifier effluent so that the product gas can be properly burned as an industrial fuel.

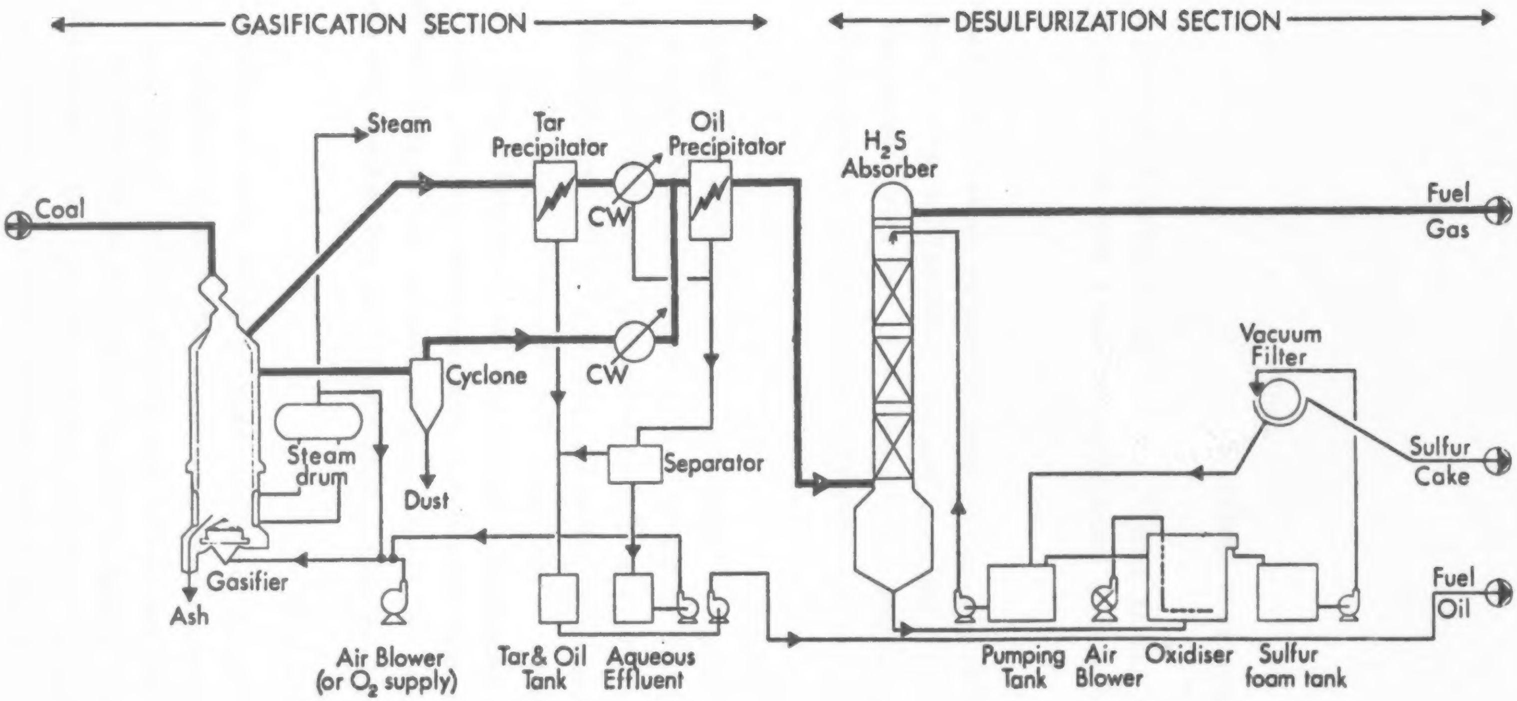
## B.5 Clean-up System on Woodall-Duckham/Gas Integrale Gasifier Effluent

The principle of Woodall-Duckham/Gas Integrale (WD/GI) two-stage coal gasification is to separate the volatile matter of the coal before subjecting the remainder of the coal to the high temperatures of the gasification reactions. As the coal descends through the fixed-bed gasifier, the coal is dried, then evolves gas, light hydrocarbons and tar, and reaches the bottom of the upper part of the gasifier as semi-coke, or char if the coal is a nonagglomerating coal such as sub-bituminous or lignite.

The semi-coke or char now passes into the gasification zone, where temperatures rise from about 1200°F at the side gas off-take to typically 2200°F at the final combustion stages.

The gasification agent converts the semi-coke into carbon monoxide, carbon dioxide, hydrogen, some undecomposed steam and nitrogen. This product is termed clear gas. About half the clear gas is withdrawn at 1200°F via the side gas off-take, the remainder passing overhead to dry and devolatilize the coal.

This split-flow system, together with a very low gas off-take velocity, keeps fines carryover to a very low level. Very low fines carryover is one of the features of two-stage gasification which distinguish it from single-stage gasifiers. Figure B-5.1 shows how two-stage gasification lends itself to a simple and effective gas clean-up. No direct contact scrubbing is used. The top gas at 250°F, containing all the coal volatile matter, is electrostatically detarred, indirectly cooled, and passed through a second


GASIFICATION SECTION
DESULFURIZATION SECTION
Coal
Steam
Tar Precipitator
Oil Precipitator
CW
CW
$H_2S$ Absorber
Fuel Gas
Cyclone
Steam drum
Dust
Separator
Vacuum Filter
Sulfur Cake
Gasifier
Ash
Air Blower (or $O_2$ supply)
Tar & Oil Tank
Aqueous Effluent
Pumping Tank
Air Blower
Oxidiser
Sulfur foam tank
Fuel Oil

WD/GI PROCESS FOR COLD DESULFURIZED FUEL GAS

FIGURE B-5.1

precipitator to ensure full demisting.

The clear gas at 1200°F, containing no volatile matter, is dedusted and cooled in a combination of waste heat boiler and tubular cooler.

The combined gas can be desulfurized by several well-known processes, such as the Stretford process. A Stretford unit in simplified schematic form is shown in Figure C-7.1, and this process has been used to desulfurize gas from WD/GI gasifiers to produce a sulfur cake.

Most of the sulfur contained in the coal feed will be in the product gas, mainly as $H_2S$ with 5 to 10% of the sulfur appearing as COS and $CS_2$. The $H_2S$ is easily removed in a Stretford unit to give a final product gas which can comply with $SO_2$ emission requirements for industrial fuel gas. For low-sulfur coals, $H_2S$ removal may not be necessary. Due to the low temperature predistillation of the coal obtained in the two-stage process, the product contains only traces of hydrogen cyanide (a few ppm), unlike many gases obtained from coal. This simplifies and reduces the cost of the Stretford unit.

The cooling of the sulfur-bearing gases prior to entry into the sulfur removal system produces a contaminated aqueous stream. An important feature of the process is that by using indirect cooling the volume of contaminated aqueous effluent is sharply reduced compared to direct contact cooling. This minimizes the cost of effluent disposal and, indeed, often makes simple incineration as attractive as biological treatment of this aqueous stream. Recycle of this stream to the gasifier has been practiced, but further development work is required before WD/GI feels it is appropriate to offer this process variant on future plants.

It should be emphasized that each feedstock coal presents differing operating problems. Therefore, the gas clean-up system would normally be tailored to the specific type of feedstock and may not be the same for each plant. The flow sheet shown in Figure B-5.1 does represent a design that has been reduced to practice (in South Africa). Specific gas analyses are not available, but the product gas should meet all proposed EPA guidelines for the following reasons.

Particulates:

Solids removal is effected by cyclones, electrostatic precipitators and finally by scrubbing with the acid-gas removal liquid (Stretford solution). It is highly unlikely that the fuel gas, after these successive processing steps, would exceed the particulates emission limit of 0.1 lbs per $10^6$ Btu of gas, and it most probably contains a small fraction of this amount. Particulates formed during the combustion step for low Btu gaseous fuels are generally known to be far less than 0.1 lbs per $10^6$ Btu; hence, the sum of the ash particles plus the soot particles should be less than 0.1 lbs per $10^6$ Btu.

Sulfur Dioxide:

About 90% of the sulfur-containing gas in the raw fuel gas is $H_2S$, the remaining 10% being COS and $CS_2$ with traces of mercaptans. The Stretford unit removes essentially all of the $H_2S$ but does not remove COS, $CS_2$ and the mercaptans. If it is assumed that 85% of the sulfur in a feed coal containing 3% sulfur appears in the gas product, then this 10% of "organic" sulfur that is not removed will produce nearly 0.5 lbs of $SO_2$ per $10^6$ Btu when this fuel is burned. Therefore, given the suggested EPA guideline of a maximum of 0.5 lbs of $SO_2$ per $10^6$ Btu for industrial gas, it appears that coal of up to 3% sulfur can be converted to fuel gas of acceptable quality using the equipment as shown in Figure B-5.1. Use of coals higher than 3% sulfur may require the partial removal of organic sulfur compounds (in addition to removal of $H_2S$) in order to meet the emissions requirement guideline. Some processes are available to meet this requirement.

The $NO_x$ content of combusted gas is determined mostly by flame temperature, excess air and the chemically-bound nitrogen in the fuel itself. Because the theoretical flame temperature of the WD/GI fuel gas is some 200°F colder than high-Btu (natural) gas, the thermal fixation of $NO_x$ should be reduced. Fuel-bound nitrogen, if present, should exist in the converter effluent gas as HCN and $NH_3$ with only traces in the HCN form. $NH_3$ will probably be found in varying amounts, depending on the quality of the coal, time-temperature history of the coal particle, and hydrogen partial pressure. Not all of this ammonia will end up as $NO_x$ because some ammonia is removed by the gas clean-up as an aqueous condensate and various studies show limited combustion of the remainder to $NO_x$. Thus, it is believed that $NO_x$ formation from this fuel gas will be substantially below the guideline emission level of 0.4 lbs of $NO_x$ per $10^6$ Btu.

The presence of water vapor in a gas is also known to lower the formation of $NO_x$ during the combustion process due to a cooler flame. WD/GI gas normally contains an appreciable amount of water vapor because it is saturated with water at about 100°F or higher. Therefore, the beneficial effect of decreased $NO_x$ formation is generally realized when this gas is burned.

Commercial Operations:

The commercial operations of several WD/GI units to produce synthesis gas for ammonia or methanol synthesis are further proof that gas clean-up methods have been developed to adequately purify coal-derived gases to a degree of purity higher than required by industrial fuel gas. The sulfur and particulate contents of synthesis gas must be essentially zero in order to avoid the poisoning of catalysts; hence, gas clean-up to less stringent criteria would appear to be demonstrated. This is not to say that significant improvements cannot be made, but coal-derived gases can be purified.

## SECTION C - COMPARISON OF IRON-BASED CLEAN-UP PROCESS AND THE STRETFORD PROCESS

1. Introduction
2. Development of Gas Clean-up Processes
   - 2.1 Iron Oxide Box Purifiers
   - 2.2 Liquid-phase Iron Oxide Processes
   - 2.3 Stretford Process
3. Basic Chemistry
   - 3.1 Iron Oxide Box Process
   - 3.2 Liquid-phase Iron Oxide Processes
   - 3.3 Stretford Process
4. Design Basis and Assumptions
5. Iron Oxide Box Purifiers
   - 5.1 Design Based on American Practice
   - 5.2 Design Based on European Practice
   - 5.3 Discussion
   - 5.4 Advantages and Disadvantages
6. Liquid-phase Iron Oxide Processes
   - 6.1 Process Description
   - 6.2 Process Requirements
   - 6.3 Advantages and Disadvantages
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   - 7.1 Process Description
   - 7.2 Process Requirements
   - 7.3 Advantages and Disadvantages

## C.1 Introduction

Recent interest in gas clean-up has generally been directed toward the use of processes which almost completely remove pollutants because of the stringent standards necessary for pipeline gas or synthesis gas. With revived interest in industrial gas generation, a new prospect to be considered is a reexamination of old technology. This type of process may not be so complex or costly and may be applied if a lower percentage of sulfur removal is satisfactory as is the case of industrial fuel compared to pipeline gas. Processes possibly falling into this category are those based on iron oxide and a great deal of information on both the iron oxide box and liquid versions are given in Kohl and Riesenfeld's text (Iron Oxide Process Reference #3). This section, therefore, will consider the old and new technologies that might be applied to make industrial gas by comparing designs of older iron oxide processes with the Stretford process as the representative of modern day development. Either way, the sulfur level can be brought within the guideline level of 0.5 lbs of $SO_2$ per $10^6$ Btu for industrial fuels while making elemental sulfur directly without a Claus unit.

Iron oxide boxes are one of the oldest methods for gas purification still in industrial use. The engineering design of units for industrial gas clean-up is possible from publicly available sources of information. American and European practices differ and the results of both are presented.

Improvements of the iron oxide process to save on space requirements and labor and to recover sulfur resulted in the development of a continuous liquid-phase sulfur clean-up system. The economic factors that promoted this development are still valid today when cleaning industrial gas. Thus, a generalized combination of the Ferrox, Gluud and Manchester iron-oxide-based liquid-phase processes was used for a process design comparison case.

## C.2 Development of Gas Clean-up Processes

### 2.1 Iron Oxide Box Purifiers

The iron oxide process was introduced in England around the middle of the 19th century. Before that time, a wet purification process utilizing calcium hydroxide as the active agent was used. Although iron oxide processes are still used on a large scale for treatment of coal gases, recently developed wet purification processes have gradually been replacing oxide box purifiers.

A simple form of the dry-box process utilized for the first batch-type installations completely removed hydrogen sulfide with hydrated ferric oxide. At the completion of a cycle, ferric sulfide formed in the reaction is oxidized to elemental sulfur and ferric oxide by exposure to air. Hydrogen sulfide is oxidized to elemental sulfur and water in the overall chemical reaction. The cycle is repeated until sulfur fills most of the pores and coats most surfaces with tar and sulfur. Then the bed is less active, pressure drop increases and the bed must be removed from the box for cleaning. The oxide was often reused after the sulfur had been removed. Any current applications of this process must dispose of the tar and sulfur laden spent oxide not suitable for regeneration in a way compatible with present environmental standards.

More economical revivification methods were discovered later. In one, the iron is revivified continuously by addition of small amounts of air or oxygen to the purification plant inlet gas. The other method involves a cyclic in situ revivification by circulation of oxygen-containing gas after the bed has been fouled. Eventually, the iron oxide bed must be removed to avoid excessive back pressure and to maintain good gas contact. Benefits of the revivification improvements were a savings due to reduced frequency of loading and unloading and the achievement of a higher level of sulfur content before it was necessary to dispose of the iron oxide batch.

### 2.2 Liquid-phase Iron Oxide Processes

Since the main disadvantages of dry iron oxide purification are large ground space requirement, high labor costs of the purification plants and the disposal of a large quantity of spent iron oxide, a search for more efficient methods for hydrogen sulfide removal from the gases was undertaken. This search resulted in the development of the liquid-phase iron oxide processes. A logical step employed liquids in regenerative cycles and utilized reaction between iron oxide and hydrogen sulfide followed by conversion of iron sulfide to iron oxide and elemental sulfur. Starting with the work of Burkheiser shortly before the first World War, several processes which were developed in Europe and the United States used iron oxide suspended in alkaline aqueous solutions. The Koppers Company of Pittsburgh introduced the Ferrox process in the 1920's. Gluud introduced a similar process in Germany. In England, a more recent modification of the Ferrox process, known as the Manchester process, was introduced.

Use of these processes has been diminishing to some extent. At present the Burkheiser process is not in commercial use although a new proposal for a novel coal-gas purification scheme has been made. While a few Ferrox plants are still operating in the United States, most have been replaced by more modern systems. The Gluud process still finds some use. In Great Britain, where the Manchester process was popular, the Stretford process covered later in this section is replacing it.

### 2.3 Stretford Process

The Stretford process was developed in the early 1960's by the Western Gas Board and the Clayton Aniline Company for removal of hydrogen sulfide from coal gas. Initially, an alkaline solution containing the sodium salt of 2-6 and 2-7 anthraquinone disulfonic acid (ADA) absorbed $H_2S$ and converted it to sulfur. Due to the excessively long reaction time between $H_2S$ and ADA, equipment sizes were large and the solution had an excess dissolved salt accumulation. The discovery of adding vanadate salts to the alkaline ADA solution reduced the reaction time. The vanadium salt participates as an oxidizing agent which ADA later restores to the oxidized form.

## C.3 Basic Chemistry

### 3.1 Iron Oxide Box Process

The following equations illustrate the chemistry involved in iron oxide purification:

Absorption: $Fe_2O_3(H_2O)_x + 3\ H_2S = Fe_2S_3 + (x+3)\ H_2O + \text{heat}$

Revivifying: $2\ Fe_2S_3 + 3\ O_2 + x\ H_2O = 2\ Fe_2O_3(H_2O) + 6\ S + \text{heat}$

Overall Reaction: $2\ H_2S + O_2 = 2\ H_2O + 2\ S + \text{heat}$

Depending on operating conditions, a large number of other reactions may occur. The reaction mechanism is principally influenced by temperature, moisture content, and pH of the purifying material.

Both, mixed and unmixed, iron oxides are used for gas-purifying materials. Both types contain iron oxide that may be prepared by the air oxidation of iron borings in the presence of water and lime. The make-up of each class follows:

Unmixed oxide - pure hydrated ferric oxide and sometimes fibrous materials such as those occurring in natural iron oxides ores.

Mixed oxide - artifically prepared by supporting finely divided iron oxide on materials of large surface and loose texture such as wood shavings and granulated or crushed slags.

Mixed oxides have the following advantages:

Control of bulk density, iron oxide content, moisture and pH.

Reduced tendency to cake.
Free passage of gas.
Higher final sulfur loading

Capacity and activity are two important aspects in the selection of purifying materials. In theory, 0.64 lb of hydrogen sulfide will react with 1 lb of anhydrous ferric oxide, but only up to about 0.56 lb sulfur/lb ferric oxide has been achieved in operations. Capacity decreases progressively with every cycle after the first.

## 3.2 Liquid-phase Iron Oxide Processes

The chemistry involved in the liquid-phase processes is based on the reaction of $H_2S$ with either sodium carbonate or ammonia and the subsequent reaction of the hydrosulfide formed with iron oxide. Regeneration follows by aerating the iron sulfide and converting it to iron oxide and elemental sulfur. The reaction mechanism for the process using iron oxide suspended in an alkaline aqueous solution is shown by the following equations:

$$H_2S + Na_2CO_3 = NaHS + NaHCO_3$$

$$Fe_2O_3 \cdot 3\,H_2O + 3\,NaHS + 3\,NaHCO_3 = Fe_2S_3 \cdot 3\,H_2O + 3\,Na_2CO_3 + 3\,H_2O$$

$$2\,Fe_2S_3 \cdot 3\,H_2O + 3\,O_2 = 2\,Fe_2O_3 \cdot 3\,H_2O + 6\,S$$

Several, mostly undesirable, side reactions occur depending on the operating conditions and the composition of the gas to be treated. Some thiosulfate formation is inevitable and it has been reported that sometimes it may even be desirable to completely convert to thiosulfate as follows:

$$2\ NaHS + O_2 = Na_2S_2O_3 + H_2O$$
$$Na_2S + 1\text{-}\tfrac{1}{2}\ O_2 + S = Na_2S_2O_3$$

Another undesirable side reaction occurs when hydrogen cyanide absorbed in the alkaline material is converted to thiocyanate. The mechanism first involves formation of sodium cyanide which is then oxidized by elemental sulfur as follows:

$$HCN + Na_2CO_3 = NaCN + NaHCO_3$$
$$NaCN + S = NaSCN$$

Not all of the HCN is converted because a majority is stripped from solution by regeneration air.

Significant concentrations of hydrogen cyanide in the gas can possibly lead to a mechanism in which the iron oxide reaction with hydrogen sulfide is inhibited. Noticeable color changes have been observed in the solution when treating a gas in which hydrogen cyanide approaches 10% of the hydrogen sulfide concentation. Oxidized solution has a blue coloration due to the presence of ferric-ferrocyanide complexes which become pale yellow in the fouled condition. While reaction between iron oxide and hydrogen sulfide is quite slow, the blue complexes support rapid conversion of hydrogen sulfide to sulfur. It is hypothesized that the reactions involve oxidation of $H_2S$ by conversion of the ferric-ferrocyanide complex to ferrous ferrocyanide. Ferric-ferrocyanide is reestablished in the regeneration step. The reactions can be represented by the following equations:

$$2\ H_2S + Fe_4(Fe(CN)_6)_3 + 2\ Na_2CO_3 =$$
$$2\ Fe_2Fe(CN)_6 + Na_4Fe(CN)_6 + 2\ H_2O + 2\ CO_2 + 2\ S$$

$$2\ Fe_2Fe(CN)_6 + Na_4Fe(CN)_6 + 02 + 2\ H_2CO_3 =$$
$$Fe_4(Fe(CN)_6)_3 + 2\ Na_2CO_3 + 2\ H_2O$$

Iron, lost with the sulfur as iron cyanide compounds, is replenished with a dissolved solution of iron sulfate.

## 3.3 Stretford Process

Hydrogen sulfide is absorbed into a solution consisting mainly of sodium metavanadate, sodium anthraquinone disulfonate (ADA), sodium carbonate and sodium bicarbonate in water. Sodium carbonate reacts with the $H_2S$ to produce sodium hydrosulfide as follows:

$$H_2S + Na_2CO_3 \longrightarrow NaHS + NaHCO_3$$

Free sulfur is formed by oxidation with sodium metavanadate. Vanadium in this reaction is reduced as shown:

$$HS^- + 2\ V^{5+} \longrightarrow 2V^{4+} + S + H^+$$

The full reaction equation is:

$$2\ NaHS + 4\ NaVO_3 + H_2O \longrightarrow Na_2V_4O_9 + 2\ S + 4\ NaOH$$

Vanadium is reoxidized by reacting with ADA in the oxidizer as follows:

$$2\ V^{4+}\ \text{ADA (oxidized)} \longrightarrow 2V^{5+} + \text{ADA (reduced)}$$

or:

$$Na_2V_4O_9 + 2\ NaOH + H_2O + 2\ \text{ADA} \longrightarrow 4\ NaVO_3 + 2\ \text{ADA (reduced)}$$

Unused caustic (4 moles formed in the vanadium reduction equation and only 2 moles are consumed in the previous equation) reacts with sodium bicarbonate:

$$2(NaOH + NaHCO_3 \longrightarrow Na_2CO_3 + H_2O)$$

The reduced form of ADA is oxidized by air blowing:

$$2\ \text{ADA (reduced)} + O_2 \longrightarrow 2\ \text{ADA} + 2\ H_2O$$

Overall, the above combination of reactions reduces to:

$$2\ H_2S + O_2 \longrightarrow 2\ S + 2\ H_2O$$

Side reactions include oxidation of sodium hydrosulfide to thiosulfate, conversion of hydrogen cyanide to sodium thiocyanate, and formation of sodium sulfite and sulfate from $SO_2$.

$$2\ NaHS + 2\ O_2 \longrightarrow Na_2S_2O_3 + H_2O$$

$$2\ HCN + 2\ NaHS + O_2 \longrightarrow 2\ NaCNS + 2\ H_2O$$

$$SO_2 + 2\ Na_2CO_3 + H_2O \longrightarrow Na_2SO_3 + 2\ NaHCO_3$$

$$2\ Na_2SO_3 + O_2 \longrightarrow 2\ Na_2SO_4$$

## C.4 Design Basis and Assumptions

As a comparison of requirements to remove hydrogen sulfide from product gas of a typical gasifier, the following calculation basis and assumptions have been made:

1. $4 \times 10^9$ Btu/day capacity of coal gasification plant.
2. Heating value of gasification product gas is 175 Btu/SCF.
3. Assume particulate and tars in the product gas have been removed before the gas enters into a hydrogen sulfide removal system.
4. Use 3.0 W % sulfur coal.
5. Assume all sulfur in coal appears mole for mole in the product gas (conservative assumption).
6. Assume thermal efficiency of a gasification process is 80%.
7. Assume heating value of coal is 12,500 Btu/lb.

Calculation of sulfur content of product gas:

12,500 Btu/lb of coal x 80% = 10,000 Btu in product gas/lb coal
4,000,000,000/10,000 = 400,000 lbs of coal/day
= 200.0 tons of coal/day
10,000/175 = 57.14 SCF product gas/lb of coal
0.03 lb sulfur in coal/32 lb/mole = 0.0009375 moles sulfur compounds in gas (assuming 100% recovery of sulfur in coal)
= 0.3562 SCF of sulfur compounds in gas per lb of feed coal
= 0.619 V % concentration of sulfur compounds in product gas
= 6190 ppm by volume

4,000,000,000/175 = 22,857,000 SCFD of product gas

= 952,380 SCFH

0.03 lb sulfur x 7000 grains/lb = 210 grains sulfur compound in gas per 57 SCF product gas

= 368 grains/100 SCF of unpurified product gas

## C.5 Iron Oxide Box Purifiers

### 5.1 Design Based on American Practice

Bed Size Estimation -

Empirical rules, for the most part, provide the process design method for iron oxide bed purifiers. The Steere Engineering Co. has proposed the most commonly used method in the United States. The formula is expressed by the following equation:

$$A = \frac{GS}{3{,}000\ (\ D + C\ )}$$

where:

A = cross-sectional area of gas flow through any one box, in series, of a set.

G = maximum gas rate, SCF/hr.

S = correction factor determined by the hydrogen sulfide content of the inlet gas.

D = total depth of oxide in feet through which the gas will pass in the purifier set. In split flow designs where half the gas volume passes through each layer, the gas flow area is twice the cross-sectional area of the box, while D is the depth of one layer of oxide.

C = factor determined by the number of boxes as follows: 4 for 2 boxes; 8 for 3 boxes; and 10 for 4 boxes.

The values of the S correction factor are:

| Grains $H_2S$/100 SCF of Unpurified Gas | Factor |
|---|---|
| 1000 or more | 720 |
| 900 | 700 |
| 800 | 675 |
| 700 | 640 |
| 600 | 600 |
| 500 | 560 |
| 400 | 525 |
| 300 | 500 |
| 200 or less | 480 |

The influence of $H_2S$ loading may be observed from the graphical presentation of this data in Figure C-5.1.

Estimated Box Purifier Design -

Detailed calculations are given in the Appendix.

| | | |
|---|---|---|
| No. of iron oxide boxes | | 10 |
| Unit Size: | Square | 37 ft x 37 ft x 10 ft high |
| | Circular | 41 ft I.D. x 10 ft high |
| Gas Volume (Inlet) | | 22.86 million cu ft/day<br>(4 x $10^9$ Btu/day) |
| $H_2S$ Content | (Inlet) | 368 grains/100 SCF gas |
| | (Outlet) | 29 grains/100 SCF gas |

5.2 Design Based on European Practice

Bed Size Estimation -

The space velocity through one box, known at the R ratio, governs European oxide-purifier design. Selected values of R may be applied in the space velocity equation given below to design box size.

$$R = \frac{\text{cubic feet of gas per hour}}{\text{cubic feet of oxide in one box}}$$

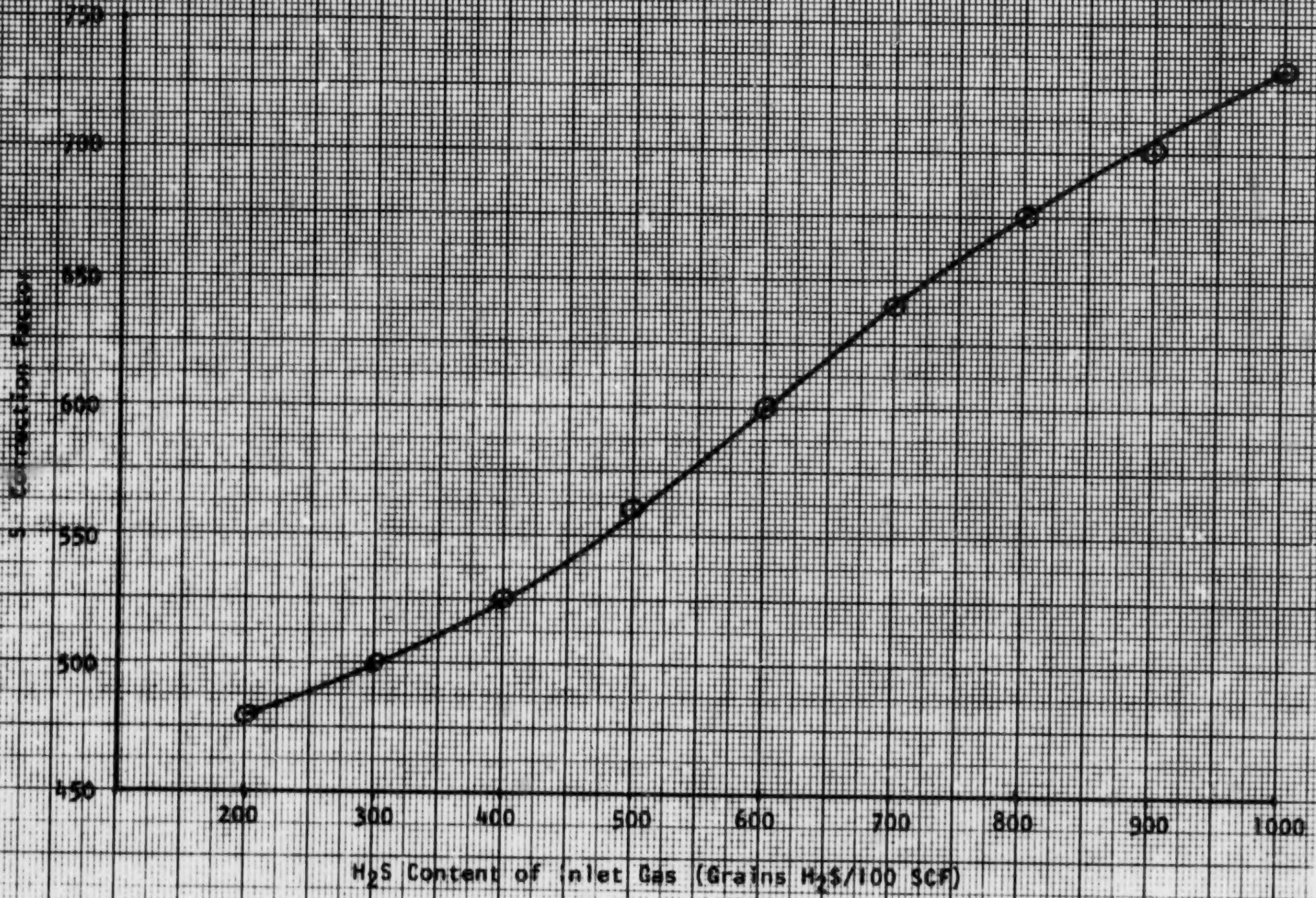
R values can be varied from 15 for a conservative design to as high as 100 for some installations. Good design practice for systems operating at essentially atmospheric pressure and with revivification in situ use an R ratio of 20 to 50.

Minimum standards of the oxide-purifier design require an oxide bed to be at least 10 feet deep to produce sufficient pressure drop for proper gas distribution over the entire cross-sectional area. Also, vessel diameter should limit deposition to a maximum of 15 grains/square foot of cross-sectional area of bed per minute.

K·E 10 X 10 TO THE CENTIMETER 18 X 25 CM.
KEUFFEL & ESSER CO. MADE IN U.S.A.
46 1513

FIGURE C-5.1

IRON OXIDE DESIGN FACTOR CHART (AMERICAN PRACTICE)



Estimated Box Purifier Design -

Detailed calculations are given in the Appendix.

| | | |
|---|---|---|
| No. of iron oxide purifiers | | 4 |
| Unit Size: | Square | 35 ft x 35 ft x 10 ft high |
| | Circular | 39 ft I.D. x 10 ft high |
| R Factor | | 20 |
| Gas Volume (Inlet) | | 22.86 million cu ft/day<br>(4 x $10^9$ Btu/day) |
| $H_2S$ Content | (Inlet) | 368 grains/100 SCF gas |
| | (Outlet) | 29 grains/100 SCF gas |

## 5.3 Discussion: Dry Iron Oxide Process

The iron oxide box purification process provides reliable and effective hydrogen sulfide removal. Its space requirement, however, may be excessive and the operation produces a considerable quantity of spent iron oxide (when revivification is not effective) which must be disposed. The limiting factor in the iron oxide process is that it requires a large ground space. This may rule out many large existing plants.

Hydrogen sulfide removal in iron oxide box purification is a surface reaction. Dust, light oils, naphthalene, and tars should be removed before purification since these materials coat the iron oxide and render it unreactive. For optimum operation of the process, the gas should not contain more than 0.4 grain per 100 cubic feet of tars, oils and dust. This low tar loading requirement may limit the application of the iron oxide purification process to some gasification processes since they produce significant amounts (about 10 W %) of tars and light oils per pound of feed coal.

## 5.4 Advantages and Disadvantages of the Dry Iron Box Process

Advantages -

1. Completely removes small to medium concentrations of hydrogen sulfide without removing carbon dioxide.
2. Equally effective at any operating pressure.
3. Removes mercaptans or converts them to disulfides.
4. Produces a final product in elemental sulfur form.
5. Well proven commerical process.

Disadvantages -

1. A batch process, requiring duplicate installations or flow interruption of process gas.
2. Requires large ground space for large gas plants.
3. Hydrogen cyanide reacts irreversibly with iron oxide causing a loss of purifying material.
4. The iron oxide sponge bed may become coated with entrained oil, tar or distillates and require more frequent changing. Thus, it may be necessary to wash the gas with oil (e.g., benzene scrubber) before iron oxide box purification.
5. High labor cost.
6. Disposal of a large quantity of iron oxide sponge from spent beds is necessary.

## C.6 Liquid-phase Iron Oxide Processes

### 6.1 Process Description

The schematic flow diagram of a liquid-phase iron oxide process is shown in Figure C-6.1. The system consists of a packed column (absorber) and a regenerator. Scrubbing solution, normally containing 3.0 W % $Na_2CO_3$ and 0.5 W % ferric hydroxide, is pumped to the top of the absorber where it is counter-currently contacted with the raw product gas fed into the bottom of the vessel. The liquid is circulated at such a rate that a two to threefold excess of ferric hydroxide over the stoichiometric quantity necessary for the complete reaction with hydrogen sulfide is present.

The hydrogen sulfide-containing solution flows from the bottom of the absorber to the regenerator. Elemental sulfur, formed in the regenerator by contact of the solution with air, accumulates as a froth on the liquid surface, flows to the slurry tank, and is pumped from there to a filter where excess liquid is removed. A part or all of this liquid may be discarded, thereby purging undesirable salts from the system. Oxidized solution is pumped from the regenerator back to the absorber to complete the cycle. Foul gas from the oxidizer is vented to either a boiler or a washer.

### 6.2 Process Requirements

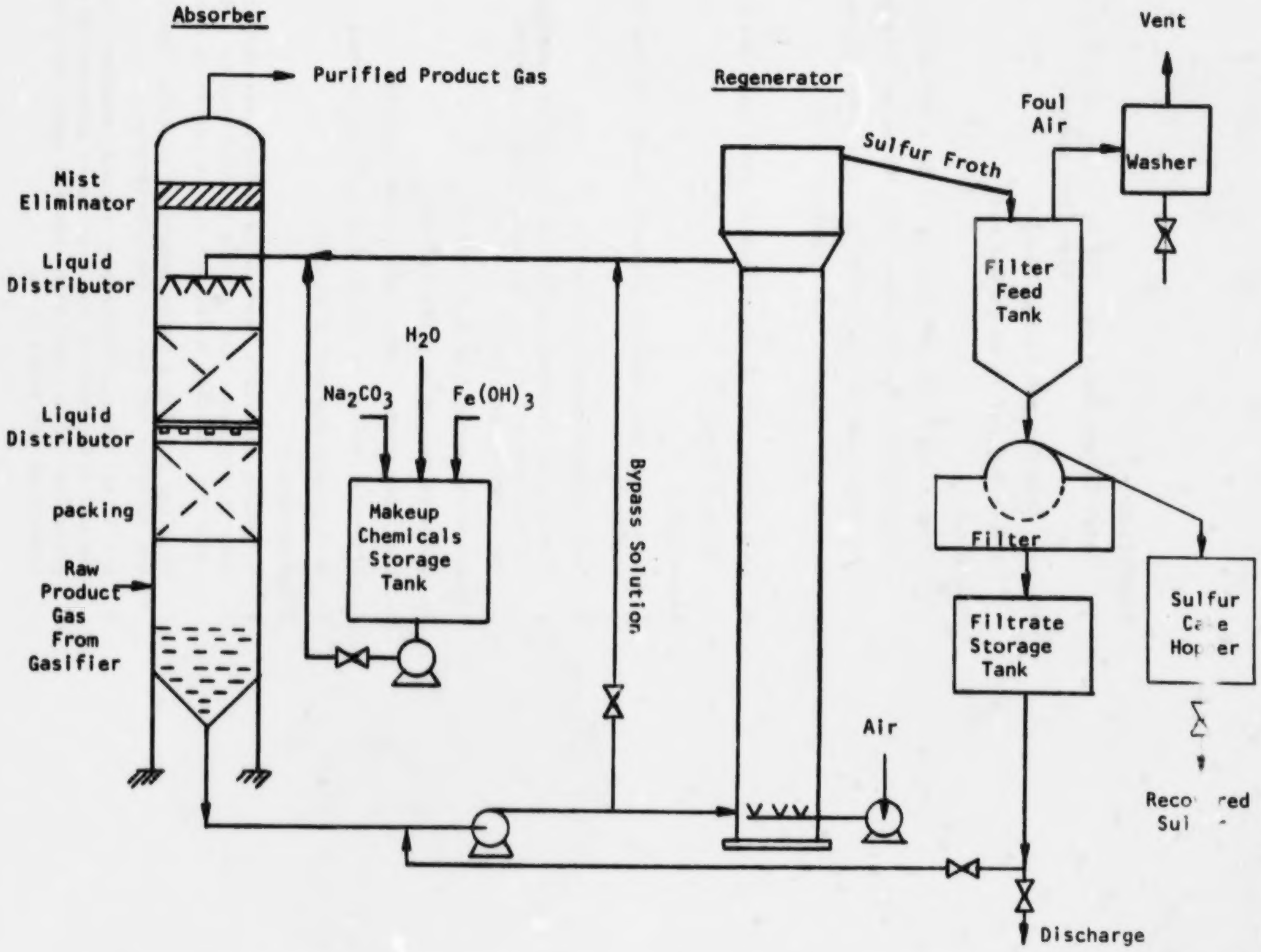
The estimated sizes of the equipment for treating 4 x $10^9$ Btu per day of low-Btu gas (175 Btu/SCF) are:

Packed Tower -

| | |
|---|---|
| Packed Column: | 9 ft 3 in I.D. x 50 ft overall height |
| Packing Height: | 26 ft |
| Packing Material: | 2" Intalox saddles with $F_p = 40$ |

FIGURE C-6.1

FLOW DIAGRAM OF LIQUID IRON OXIDE PROCESS FOR $H_2S$ REMOVAL


Absorber
Purified Product Gas
Mist Eliminator
Liquid Distributor
Liquid Distributor
packing
Raw Product Gas From Gasifier
$H_2O$
$Na_2CO_3$
$Fe(OH)_3$
Makeup Chemicals Storage Tank
Bypass Solution
Regenerator
Air
Sulfur Froth
Foul Air
Vent
Washer
Filter Feed Tank
Filter
Filtrate Storage Tank
Sulfur Ca e Hop er
Reco red Sul
Discharge

Regenerator -

Total Volume Required: 777 $ft^3$, i.e., 7.0 ft x 20 ft high (for example)

Pressure Drop Through Packed Tower -

0.5 in $H_2O$ per ft of packed bed

Flow Rates -

Product Gas: 952,380 SCFH or 22.86 x $10^6$ SCFD

Solution Circulation Rate: 165 lb/sec or 1161 gpm

Air Requirement: 815 SCFM (2x stoichiometric amount)

Detailed calculations are shown in the Appendix.

### 6.3 Advantages and Disadvantages of the Liquid-phase Iron Oxide Process

Advantages -

1. Continuous gas clean-up process, using inexpensive chemicals.
2. Small ground space requirement.
3. Flexible to accommodate the variations of hydrogen sulfide content of the raw gas. Easy to control the process operation.
4. Selective removal of $H_2S$ from $CO_2$.
5. Operates over wide pressure ranges.
6. Low labor cost; little supervision required.
7. Elemental sulfur is produced as a final product.
8. Well proven commercial process.

Disadvantages -

1. Scrubbing chemicals react with HCN irreversibly to produce thiocyanates and to form thiosulfates by side reactions, causing a loss of active purifying material.
2. Requires pumping a large amount of recycle liquid to the absorber and air to the regenerator.
3. $H_2S$ is not always completely removed; however, the $H_2S$ removal efficiency of the process is adequate to meet projected EPA air pollution control guidelines for industrial gas users.

4. Like any other liquid-phase $H_2S$ removal process, the corrosion problems must be surmounted.
5. Bleed-off liquid streams must be treated before discharge. The streams contain sodium thiocyanate, thiosulfates, sodium carbonates and ferric hydroxide.
6. Does not remove most organic sulfur compounds.
7. Operates at low temperatures, ambient to 100°F.

## C.7 The Stretford Process

### 7.1 Process Description

As shown in Figure C-7.1, feed gas to be purified is scrubbed in an absorber by a counter-current flow of an alkaline solution at about 80°F to 100°F. The solution, containing a vanadium salt along with an anthraquinone derivative, oxidizes $H_2S$ into elemental sulfur while the vanadium is reduced. To insure complete precipitation of sulfur, a delay tank beneath the absorber retains the Stretford solution for 10 to 20 minutes. The solution reaches an equilibrium with respect to the carbon dioxide in the gas and only relatively small amounts of $CO_2$ are removed by the process.

Liquor from the absorber is fed to oxidizers to restore vanadium to the oxidized form through a mechanism involving oxygen transfer via the anthraquinone derivative. Air blown through the oxidizer also separates sulfur by froth flotation. The scum produced is either filtered or centrifuged, washed, and melted into high-quality sulfur.

### 7.2 Process Requirements

$H_2S$ removed from raw product gas to meet the study basis guideline (952,380 SCF/hr gas, 3.68 gr $H_2S$/SCF, 92% removal):

0.128 lb $H_2S$/sec

Stoichiometric $Na_2CO_3$ requirement to convert $H_2S$ ($Na_2CO_3 + H_2S = NaHS + NaHCO_3$):

3.118 lb $Na_2CO_3$/lb $H_2S$

or

0.399 lb $Na_2CO_3$/sec

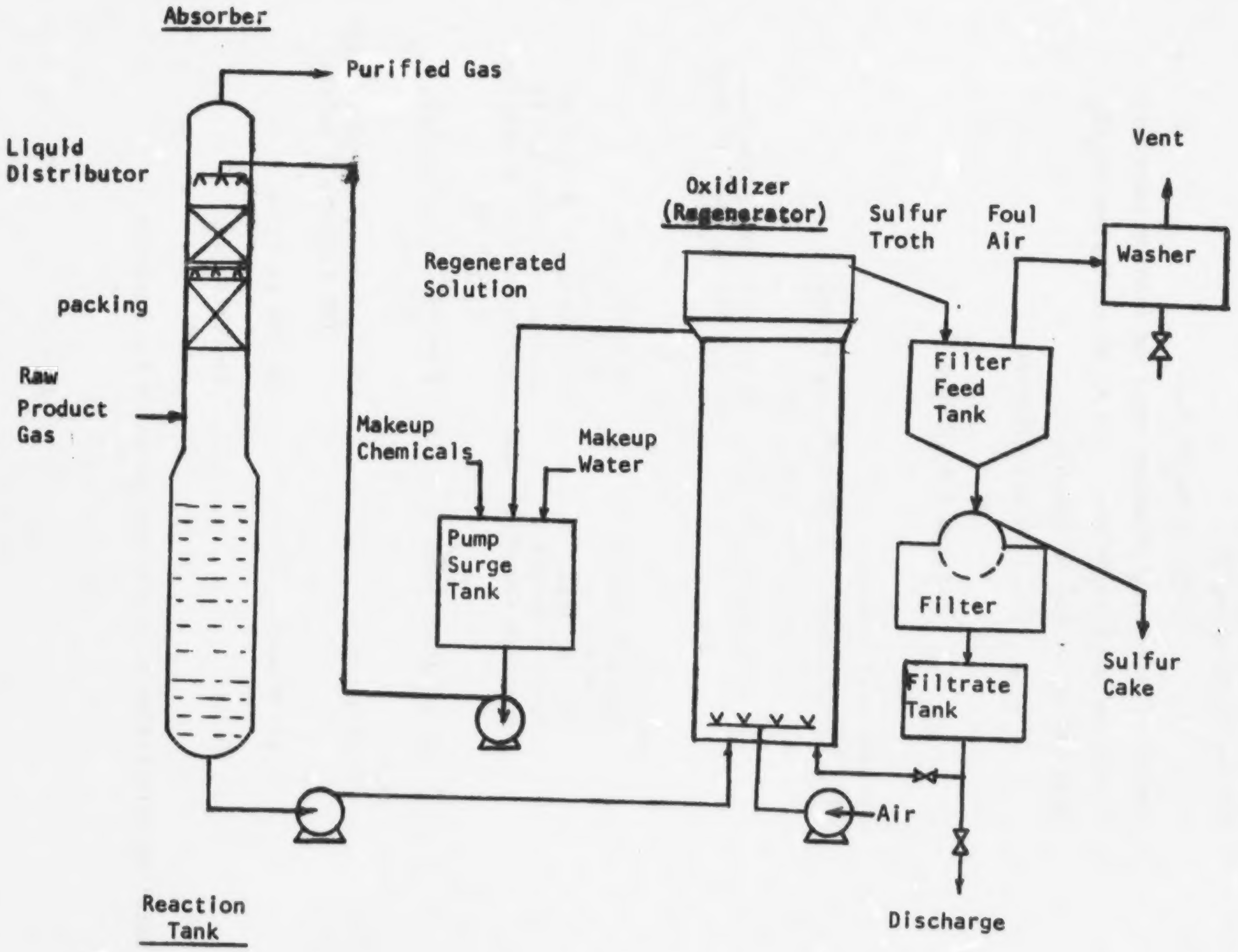

Absorber
Purified Gas
Liquid Distributor
packing
Raw Product Gas
Reaction Tank
Makeup Chemicals
Regenerated Solution
Makeup Water
Pump Surge Tank
Oxidizer (Regenerator)
Sulfur Troth
Foul Air
Vent
Washer
Filter Feed Tank
Filter
Sulfur Cake
Filtrate Tank
Air
Discharge

FIGURE C-7.1

FLOW DIAGRAM OF STRETFORD PROCESS

Practical $Na_2CO_3$ requirement (usually two to three times theoretical; using 3):

1.197 lb $Na_2CO_3$/sec

Amount of scrubbing solution required (sodium carbonate: 0.1 N; sodium bicarbonate: 0.3 N, or equivalent $Na_2CO_3$ solution of 0.505% by weight):

237.1 lb solution/sec

or

1625 gpm @ 65.5 lb/ft$^3$

Process Unit Summary -

Raw Gas Rate: 22.86 x $10^6$ cu ft/day

$H_2S$ in, grains/100 SCF: 368

$H_2S$ out, grains/100 SCF: 29 (to meet EPA guidelines of 0.5 lbs $SO_2$ per $10^6$ Btu)

| | |
|---|---|
| Absorber | |
| Overall Height | 85 ft (about) |
| Diameter | 10 ft I.D. |
| Packing Type | 2" saddles with $F_p$ = 40 |
| Packing Height | 2 sections each 16.5 ft |
| Reaction (Holding) Tank | Bottom section of absorber 27 ft high |
| Circulation Pump | 2 Units (one stand-by), 1625 gpm |
| Oxidizer | 14 ft 6 in I.D. x 20 ft high (25 ft overall height) |
| Air Blower | 60,000 ct ft/hr |
| Filter | Vacuum Rotary |

Detailed calculation estimates are given in the Appendix.

## 7.3 Advantages and Disadvantages of the Stretford Process

Advantages -

1. Well proven commercial process.
2. $H_2S$ removal to below 1 ppm possible.
3. Can recover $H_2S$ as pure saleable sulfur.
4. Insensitive to $H_2S/CO_2$ ratio.
5. Operates over wide pressure ranges (0 psig - 1000 psig).
6. Accepts process fluctuations.
7. Primarily mild steel construction.
8. Little supervision and maintenance required.

Disadvantages -

1. Does not remove most organic compounds.
2. Requires preprocessing for feeds which contain large quantitities of $SO_2$, HCN or heavy hydrocarbons.
3. Produces a large purge stream containing a vanadium compound, ADA, thiocyanates and thiosulfates.
4. Operates at low temperatures (ambient to 120°F).
5. Probably less economic for treating streams with an acid gas concentration greater than 15% $H_2S$ than some other processes.

## SECTION D - OPERATIONAL EVALUATION OF CONVERTER OUTPUT CONTROL SYSTEMS

1. Typical Clean-up Systems Applied to Industrial Fuel
2. Dependency of Clean-up on End Use of the Fuel Gas
3. Sulfur Emission Control with an Industrial Fuel
4. Effect of Nitrogen Compounds on Chemical Clean-up Systems
5. Tar and Oil By-products
6. Reduction of Particulates for Industrial Fuels

## D.1 Typical Clean-up Systems Applied to Industrial Fuel

The clean-up systems covered in Section B illustrate representative applications for each of the particular gasifier systems examined. Some utilize simple clean-up techniques and others are complex, but basically they all have a means to quench or cool the gas and knock out the particulate matter. Further steps required depend on the type of coal being gasified, the process conditions, and the end use of the gas.

The same considerations are, for the most part, necessary for industrial gas as for synthesis gas. Particulates and tars will have to be removed. Gas cooling, along with waste heat recovery for energy efficiency, would be appropriate. Sulfur and nitrogen removal may be necessary, although the reduction in sulfur and nitrogen levels need not be complete to reach the proposed EPA guidelines on industrial gas. These levels as suggested by the EPA are:

Sulfur - 0.5 lbs of $SO_2$ per $10^6$ Btu.
Nitrogen - 0.4 lbs of $NO_x$ per $10^6$ Btu (as $NO_2$).
Particulates - 0.1 lbs per $10^6$ Btu.

The sulfur limit may be reached through the use of the processes already discussed. Nitrogen in the form of gaseous compounds is, more or less, controlled by sulfur removal processes as discussed later. Organically bound nitrogen, in the tars and oils knocked out in the particulate and tar removal portion of the gasification systems must be given consideration to prevent pollution and this aspect is also considered later.

Carbon dioxide removal, which is required in the manufacture of pipeline gas, is not necessary for industrial fuel gas. The lower heating value of the fuel as a result of leaving carbon dioxide in the industrial gas is not likely to adversely affect most applications. In fact, a beneficial effect due to the lower flame temperature would result from a decrease in the thermal fixation of nitrogen. Of course, if a high concentration of nitrogen compounds such as hydrogen cyanide or ammonia were contained in the gas, they might have to be controlled to prevent the formation of $NO_x$.

Considering the point that the subject of this outline is control technology for industrial fuel, the ability of the illustrated systems to clean-up gas for the high standards necessary to make pipeline or synthesis gas suggests the possibility that the more tolerant requirements for industrial gas can be more easily met. The simpler systems appear to be directly applicable for industrial gas clean-up but, where inadequate, the complex systems would be able to provide the necessary performance with a relaxation of design specifications for the clean-up system. Examples of this decreased demand on acid gas clean-up requirements for industrial gas manufacture may be conveniently illustrated by calculating the effect of changed operating conditions on $H_2S$ removal with a cold methanol wash. The following three cases are estimates of an $H_2S$-bearing gas flowing in contact and at equilibrium with a cold methanol wash.

| Case | Pressure psia | Temperature °F | Approximate Methanol Circulation moles/mole $H_2S$ | Gas $H_2S$ Level ppm |
|---|---|---|---|---|
| 1 | 500 | -80 | 3200 | 0.1 |
| 3 | 500 | -60 | 3200 | 0.25 |
| 2 | 14.7 | -25 | 130 | 520 |

The first case shows the methanol circulation ratio that is necessary per mole of absorbed $H_2S$ in order to establish equilibrium with a gas containing 0.1 ppm of $H_2S$. To clean-up a gas for methanation, acid gas removal down to 0.1 ppm level would be appropriate. The effect of a refrigeration loss, as might occur due to a process upset from the loss of a compressor, would be to raise the gas $H_2S$ content above the desired level. Case 2 illustrates the equilibrium $H_2S$ level attained in the gas for an arbitrary was temperature rise to -60°F. While this might be an undesirable level for a methanation feed gas, it would still be more than adequate for an industrial fuel gas. Case 3 is, then, an example of how acid gas removal design criteria could be relaxed to deliver a product satisfactory for industrial fuel gas as compared to methanation feed gas. A 175 Btu per SCF higher heating value industrial fuel gas with a sulfur level of 0.5 lbs of $SO_2$ per million Btu would have about 520 ppm of $H_2S$. A methanol wash at atmospheric pressure and -25°F would be in equilibrium with this gas using a circulation of 130 moles per mole of absorbed $H_2S$.

Adapting high performance systems, capable of removing pollutants to low levels, for industrial gas clean-up may be accomplished in two ways. Naturally, one could clean up a fraction of the gas stream while bypassing the remainder in an amount such that the recombined stream would meet guidelines for an industrial fuel gas. Although such a procedure would require a somewhat smaller capacity clean-up unit (compared to treating the whole stream for synthesis), there is a good possiblity that a process design for treating the entire flow to meet requirements for an industrial gas might be advantageous. Such a consideration should be given a thorough evaluation by the designer contemplating a unit for industrial fuel manufacture. Not only is there a whole new set of design parameters for clean-up processes, but many older processes might once again be considered.

## D.2 Dependency of Clean-up Systems on the End Use of the Fuel Gas

In the final analysis, the clean-up methods used to condition the raw-gas from a gasifier are more a function of the end use for the fuel gas than it is of a particular gasification system. For example, the firing of a hot, dusty, sulfur-laden fuel gas into a cement kiln should be quite satisfactory because the cement-making process itself requires a dust control system and the limestone in the kiln feed will remove substantially all of the sulfur in the fuel. In a sense, the process provides the gas cleaning step on the raw fuel-gas and a gas of high purity is not required.

An example of an end use that is intolerant of dust is the combustion of coal-derived gas in a gas-turbine. For this application, the fuel must be extremely clean, in the order of one ppm by weight of solids. However, complete removal of sulfur is not required and the degree of sulfur removal would be dependent on local regulations governing $SO_2$ emissions.

An example of a gas requiring an intermediate degree of cleanliness with respect to dust is the mixture of coke-oven gas and blast-furnace gas that is normally used in steel mills to fire soaking pits, reheating furnaces, coke-ovens, etc. This gas is normally cleaned to a solids level of 15-30 ppm (by weight). Experience has shown that this level of cleanliness is satisfactory for distribution of gas throughout the steel mill.

Any gas containing hydrogen and carbon oxides that is to be methanated (perhaps for Btu adjustments) using a nickel catalyst must be essentially sulfur-free or contain no more than 0.1 ppm (volume) of sulfur-bearing compounds. As mentioned earlier, some industrial gas is burned without sulfur removal; hence, sulfur removal requirements can vary from no removal to complete removal in the event that catalytic processing is involved. Such a wide variance demonstrates quite clearly that the end use of a fuel-gas determines the degree of clean-up that is required provided, of course, that the final emissions meet the required EPA guidelines. This example, plus the three cases cited previously on differences in dust levels in fuel gases, confirms the importance of end use of the gas vis-a-vis the clean-up system(s) used on a given gasifier effluent.

The systems studied in Section B show this end use dependency. For the Wilputte unit, a very simple system is described because low-sulfur coal is used and the product gas is then immediately applied as a fuel. The end use in the WD/GI example, while also intended for direct use as a fuel, would tolerate medium-sulfur coals because the Stretford process was employed to remove sulfur. The Koppers-Totzek and Lurgi cases make use of the Rectisol process because further processing into ammonia and pipeline gas required a high degree of clean-up.

## D.3 Sulfur Emission Control with an Industrial Fuel

The easiest way to limit the amount of sulfur dioxide formed when combusting a coal-derived fuel gas is, perhaps, to gasify a coal sufficiently low in sulfur that the product gas, when burned, will conform to the guideline limit of 0.5 lbs of sulfur per $10^6$ Btu. Unfortunately, this method would require a feed coal containing approximately 0.25% sulfur and such coals are too rare to be of real significance. Nevertheless, the gasification of a low-sulfur fuel such as wood or wood refuse does produce a fuel gas low in sulfur, and such plants have been built and operated successfully for commercial ventures in Africa and elsewhere.

The use of low sulfur fuels such as wood is recognized by the EPA. Recently an amendment to the New Source Performance Standards was made which will affect large steam generators by allowing wood residue as a fuel supplement. The heat content of the wood residue (defined as bark, sawdust, slabs, chips, shavings, mill trim and other wood products) would be used for determining compliance with the standards so long as there is no increase in sulfur or nitrogen oxide emissions as a result. The impact of the amendment on particulate emissions has not yet been defined, and information on this subject is currently being gathered. The amendment appeared in the Federal Register on November 22, 1976 (41 FR 51397).

In Section C, some old clean-up systems used primarily for the removal of sulfur are examined and compared to a modern process. While these old systems may not compete when synthesis gas standards are required, a design is presented for comparison purposes in the manufacture of industrial gas. Depending on the particular situation under consideration, it appears from equipment requirements that the old processes might be economically attractive for some industrial gas applications.

The most practical way to remove sulfur (mostly $H_2S$) from coal-derived fuel gas is, of course, to use a one-step process that directly converts the $H_2S$ to elemental sulfur. Section C gives examples of some one-step processes. Two-step processes that selectively remove a stream rich in $H_2S$ for subsequent processing to form sulfur in a Claus-type unit are also commonly used. These two-step operations are more complex, and the tail gas from a Claus unit introduces an additional pollution stream to be cleaned-up. An idea of the difference in the complexity of the one-step versus the two-step systems can be noted in schematic flowsheets shown in Figure D-3.1. Nevertheless, the economics of two-step processing might be suitable for a large installation.

The removal of sulfur from coke-oven gas (which can be considered a special type of industrial fuel) has historically favored the one-step systems. The older liquid-phase sulfur removal systems, such as Thylox, Ferrox and Manchester, and the solid-phase iron oxide boxes are one-step processes that were so used. More recently developed one-step processes that are in use removing sulfur from coke-oven gases are:

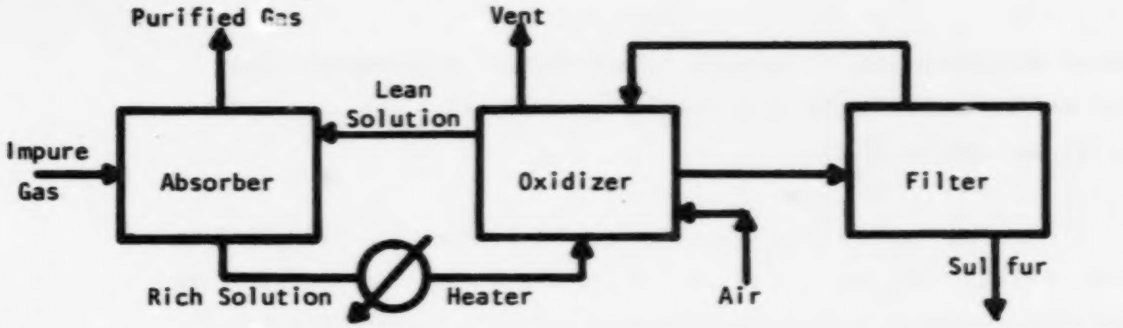
Stretford
Holmes-Stretford
Giammarco-Vetrocoke
Takahax.

The Stretford process is also being applied with modern processes. In Japan, $H_2S$ is being removed from large volumes of low-Btu gas produced in the operation of a Flexicoker.

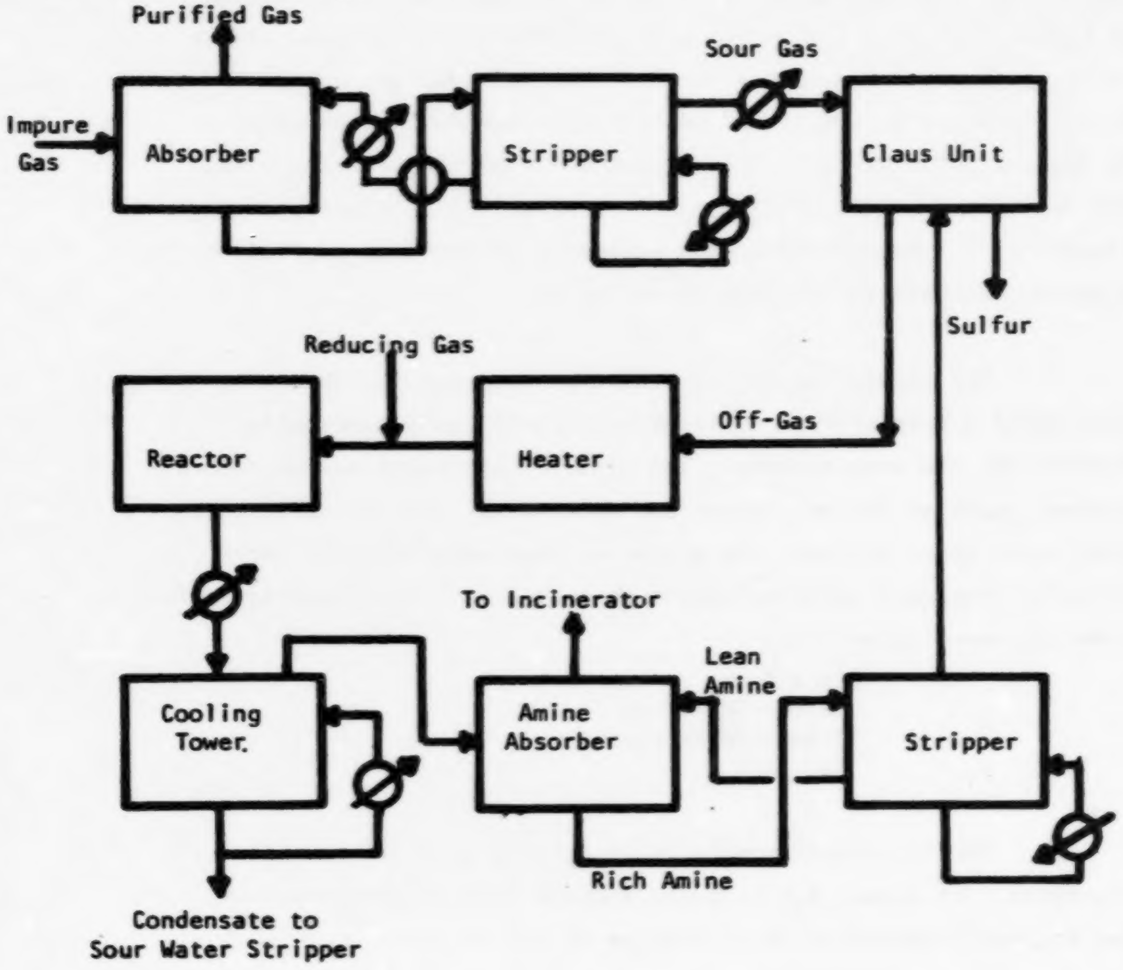
FIGURE D-3.1

FUEL GAS DESULFURIZATION SYSTEM SCHEMATIC DIAGRAMS

A. ONE-STEP SYSTEM


Purified Gas
Vent
Lean Solution
Impure Gas
Absorber
Oxidizer
Filter
Rich Solution
Heater
Air
Sulfur

B. TWO-STEP SYSTEM


Purified Gas
Sour Gas
Impure Gas
Absorber
Stripper
Claus Unit
Sulfur
Reducing Gas
Reactor
Heater
Off-Gas
To Incinerator
Lean Amine
Cooling Tower
Amine Absorber
Stripper
Rich Amine
Condensate to Sour Water Stripper

## D.4 Effect of Nitrogen Compounds on Chemical Clean-up Systems

The nitrogen content of coal, which generally runs in the range of 0.6 to 2.0 percent, can lead to problems when coal is gasified. Not only is there a risk of excessive environmental contamination, but an impact on sulfur clean-up processes may also be found. During gasification nitrogen compounds such as ammonia, cyanides, oxides of nitrogen and pyridenes may, depending on conditions, be included in the raw product gas. High temperature, for example, favors HCN but no pyridene formation.

Unfortunately, hydrogen cyanide reacts in most chemical clean-up processes to form undesirable chemicals which precipitate out of the treatment solution or are removed by purging a part of the circulating stream. In the Stretford process, almost all of the HCN will be converted to sodium thiocyanate as shown in the following equations:

$$HCN + Na_2CO_3 \longrightarrow NaCN + NaHCO_3$$
$$NaCN + NaHS + 1/2\ O_2 \longrightarrow NaCNS + NaOH$$
$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$$

or overall:

$$HCN + NaHS + 1/2\ O_2 \longrightarrow NaCNS + H_2O$$

The effluent stream purged from the process, containing thiocyanate, thiosulfate, vanadium and anthraquinone disulfonic acid, has in the past been considered an innocuous stream for disposal, but now, to meet current requirements, other methods such as recovery or biodegradation must be evaluated. In the MEA treating process, HCN can react and partially deactivate the solution. Activity of the solution can be reclaimed by treatment with sodium carbonate or caustic soda. Activated hot potassium carbonate almost completely absorbs HCN. However, the hot potassium carbonate solution is not degraded by HCN since it is removed from the solution along with $CO_2$ and $H_2S$.

When high levels of HCN are encountered, removal from the process stream may be necessary by scrubbing with a polysulfide solution. Scrubber efficiencies of over 97% can be achieved, and the HCN content of the gas can be reduced to under 30 ppm by volume. Disposal of the sodium thiocyanate, formed in the reaction between HCN and polysulfide, is necessary. As indicated for the purge solution in the previous paragraph, alternates to discarding this chemical stream must now be considered.

Ammonia dissolves in Stretford solution and can be stripped from solution during regeneration. When feed gas concentrations are above approximately 300 ppm, special precautions are necessary to prevent ammonia from being released to the atmosphere by the stripping action of regeneration air. The basic nature of ammonia makes it amenable to removal from gasifier gas in those instances of excessive ammonia concentrations. Removing ammonia from coke-oven gas by water or acid scrubbing has been the practice historically. Pyridene bases may also be scrubbed out of the gas with an acid absorbent.

## D.5 Tar and Oil By-products

The tar/oil yields on coal gasification systems are determined, to a large extent, by the intrinsic nature of the gasification system. Moving-bed counter-flow systems, such as the Lurgi, WD/GI and Wilputte gasifiers, all produce an appreciable amount of by-product liquids. On the other hand, high temperature entrained co-current gasifiers, such as Koppers-Totzek, produce no tars. The yield of these tars from the counter-flow systems, including the light-oils, represents about 4-12 wt % of the coal feed. Because the heating value of the tar/oils is higher than the heating value of the coal, the percentage of the heating value of the feed coal appearing in the tar/oil is even greater.

If the tar/oil is to be burned as a fuel, there may be problems in meeting sulfur, nitrogen and particulate specifications. Tars produced by gasification processes generally have a reduced sulfur content compared to the feed coal but have about the same nitrogen contents as the coal. A typical tar from a gasification system having a heating value of 16,500 Btu/lb requires a maximum sulfur content of 0.66 wt % to meet a specification of 0.8 lbs of $SO_2$ per $10^6$ Btu. Such sulfur contents are typical of tars produced from low to medium sulfur coals, but tars produced from high sulfur coals may have trouble meeting an emission level of 0.8 lbs of $SO_2$ per $10^6$ Btu when burned.

Information on the properties of tars produced by various gasfication systems is limited. Therefore, it is appropriate to review data from systems or equipment that simulate the conditions in a moving-bed counter-flow gasifier. Such a simulation is found in assay tests.

Assay tests for coal that distill (carbonize) coal give a clue to the sulfur content of tars as related to the sulfur content of the coal.

Assay tests on a number of different coals indicate that the sulfur content of the tar is invariably less than for the coal. These data are listed below.

DISTILLATION/CARBONIZATION ASSAY

(Bureau of Mines - Monograph 5)

| Coal Source | % S in Tar Product | % S in Coal Feed | S in Tar as % of S in Coal |
|---|---|---|---|
| Pennsylvania | 0.65 | 1.1 | 59 |
| Kentucky | 0.5 | 0.6 | 83 |
| Virginia | 0.5 | 0.6 | 83 |
| Maryland | 0.75 | 1.5 | 50 |
| Alabama | 0.7 | 0.8 | 87 |
| Pennsylvania | 0.7 | 1.0 | 70 |
| Illinois | 0.5 | 0.8 | 62 |
| British Columbia | 0.55 | 0.6 | 92 |
| Pennsylvania | 0.6 | 1.3 | 46 |
| Alabama | 0.6 | 1.1 | 55 |
| West Virginia | 0.5 | 0.6 | 83 |
| West Virginia | 0.55 | 0.9 | 61 |
| West Virginia | 0.85 | 1.8 | 47 |
| Alabama | 0.4 | 0.7 | 57 |
| Utah | 0.6 | 1.0 | 60 |
| Pennsylvania | 0.6 | 1.3 | 46 |

Some data has been found on actual gasification systems and the data tabulated below is derived from the Sythane gasification of coal (fluid-bed pressurized gasification).

## SYNTHANE GASIFICATION

| Coal Source | % S in Tar Product | % S in Coal Feed | S in Tar as % of S in Coal |
|---|---|---|---|
| Pittsburgh Seam | 0.8 | 1.5 | 53 |
| Illinois No. 6 | 2.7 | 3.5 | 77 |
| Montana Sub-bit. | 0.5 | 0.6 | 83 |
| N. Dakota Lignite | 1.0 | 1.1 | 91 |

As can be seen from all data, the sulfur content of the tar is appreciably lower than for the coal. In view of this information, it is reasonable to conclude that tars produced by any gasification process generally would have a reduced sulfur content compared to the feed coal.

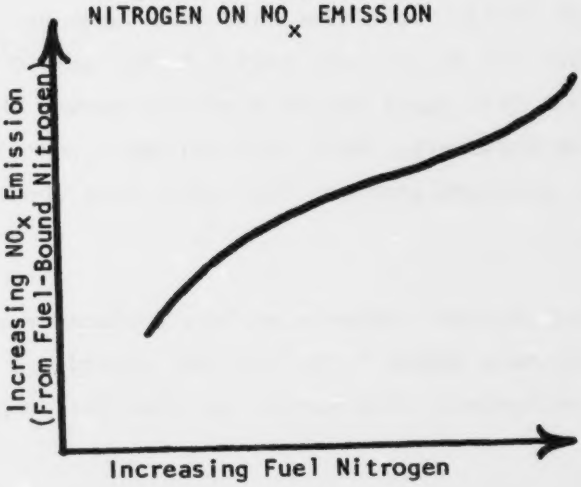
Nitrogen poses a somewhat more difficult problem. The Clean Air Act of 1971 specifies that new, large boilers have an emission level for $NO_x$ of less than 0.3 lbs. per $10^6$ Btu when firing liquid fuels. This level may be difficult to meet when firing tars produced from gasifiers. Most American coals contain 0.6-2.0% nitrogen, and the tars produced from gasifiers will have about the same amount of nitrogen.

The nitrogen contents of tars produced from most coal processing systems appear to be similar, regardless of the exact processing mechanism. This can be see from the comparison noted below.

| Type of Processing | % N in Coal | % N in By-Product Tar |
|---|---|---|
| Pressurized Fluid-Bed (Synthane) | 1.1 | 1.1 |
| In Situ Underground Gasification with Air (Hanna, Wyoming) | 0.6-0.7 | 0.74-0.79 |
| Carbonization of Illinois Coal @ 1000°C (U.S. Bureau of Mines | 1.4 | 1.1 |

When the tars are combusted, a portion of this fuel-bound nitrogen is converted to $NO_x$ and, from experiments, the general relationship between $NO_x$ and the fuel nitrogen has been determined as shown in the graph below.

EFFECT OF FUEL-BOUND NITROGEN ON $NO_x$ EMISSION



One source of data, based on the combustion of fuel oil, indicates that a fuel nitrogen content in the order of 0.35 wt % would be required to meet an emission level of 0.3 lbs of $NO_x$ per $10^6$ Btu. This is about one-third of the nitrogen content of typical tars produced from gasification systems. If this data is assumed to apply to the combustion of tar (a reasonable assumption), then tars produced in any large scale gasification project may require a hydrogenation pretreatment for the partial removal of nitrogen before the tars are burned. Such a pretreatment would also remove part of the sulfur.

An alternate disposal method would involve blending the tar into a low-nitrogen, low-sulfur fuel-oil so that the mixture, when burned, would produce pollutants at acceptable levels.

The sale of by-product tar to recover valuable chemicals obviates, of course, all of the problems associated with the combustion of tar. Such an ideal route for the disposal of tar may not always be available.

The combustion of by-product tars has been practiced by industry for many years. Special attention must be paid to the burner design because the tars will frequently contain erosive ash particles and other solids that can plug mechanical atomization devices. Steam-atomized and rotary-cup burners are generally believed to be the most trouble-free type of burner when combusting by-product tars.

## D.6 Reduction of Particulates for Industrial Fuels

The previous sections have shown a great variety of devices employed in the removal of particulates from gasifier output. In most cases, a combination of such units is used depending on the gas end use. Examples of such equipment are cyclones, spray washers, coolers and waste heat boilers (which trap tars and/or particulates in condensate), packed scrubbers, and sometimes (as in the case of iron oxide boxes) the sulfur purification process. Usually, where very low particulate levels must be achieved for applications such as synthesis gas, additional high energy removal units are also necessary. These applications might use disintegrators, venturi scrubbers or electrostatic precipitators.

Generally, data on the levels of particulate reduction accomplished through each system are not covered in the source literature. Koppers-Totzek information was an exception and particulate reduction through the various units is reported as follows:

| Unit Operation | Particulate Level (grains/SCF) | Remarks |
|---|---|---|
| Gasifier | 12 | 50-70% slag leaves bottom of gasifier; remainder is entrained. |
| Wash-Cooler | 1.2 | 90% removal of entrained particles. |
| Theisen-Irrigated Disintegrators | 0.002 | As currently recommended by Koppers Co. |
| Venturi Scrubber | 0.002-0.003 | Possible alternate to disintegrators. |
| Wet-type Electrostatic Precipitator | 0.0001 | For production of high-Btu gas. |

In the examples presented for the other units, it may be inferred that the particulate removal systems utilized are adequate for the discussed applications.

To put particulate removal necessary to meet EPA guidelines for an industrial fuel gas in perspective, the 0.1 lbs per $10^6$ Btu may be converted to 0.12 grains/SCF for a 175 Btu fuel gas. While a definition of particulate removal operations necessary to meet the guideline is not specifically covered in the literature, some generalizations can be observed. Gasifier, waste heat boiler or wash-cooler outlet particulate levels are higher than the limit, but high energy systems are excessive for the purpose of making industrial fuel gas. Possibly some combination of a cyclone, spray washer and/or packed scrubber would, in some cases, provide the necessary clean-up of particulates. In other cases, a venturi scrubber design with decreased performance requirements compared to synthesis gas might be appropriate. Depending on the Btu content of the gas made and assuming that combustion of the fuel gas adds only a negligible amount of particulates from soot formation, the clean-up system that is selected will have to remove particulates down to approximately 0.1 grain per SCF.

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# APPENDIX A

## GENERALIZED FORMULA FOR SULFUR REMOVAL FROM A FUEL TO MEET A SPECIFIC LEVEL OF $SO_2$ EMISSIONS

A formula has been derived to calculate the required percent removal of sulfur from a fuel to meet specific sulfur dioxide emissions levels in the flue gas. This equation is as follows:

$$R = 100 - \frac{1}{200}\left(\frac{EHL}{GS}\right)$$

where

E = percent efficiency of Btu recovery when processing fuel (i.e. gasification). If fuel is used directly, set E equal to 100.

G = percent of sulfur in fuel ending up in processed product which is to be burned (i.e. fuel gas from a gasifier). If fuel is burned directly, set G equal to 100.

H = high heating value of fuel, Btu/lb.

L = level of $SO_2$ contained in flue gas, lbs $SO_2$ per $10^6$ Btu.

R = percent removal of sulfur to meet desired emission level, L.

S = percent sulfur in fuel (i.e. coal to a gasifier).

An example in applying the formula to the gasification of coal and burning the product gas is as follows:

E = 75% gasifier efficiency.

G = 80% of the sulfur in coal ending up in the gasifier product.

H = 8500 Btu/lb coal heating value.

L = 0.5 lbs $SO_2$ per $10^6$ Btu (desired emission level).

S = 2% sulfur in the coal

$$R = 100 - \frac{1}{200}\left(\frac{75 \times 8500 \times 0.5}{80 \times 2}\right) = 90.04\% \text{ sulfur removal required.}$$

# APPENDIX B

## SAMPLE CALCULATIONS OF CLEAN-UP PROCESSES

NOTE: Basis, assumptions and basic calculations are stated in Section C.

### 1. Dry Iron Oxide Purifiers

#### A. Design Based on American Practices

$G = 952{,}380$ SCFH

$S = 515$ (factor for 368 grains per 100 SCF gas)

EPA air pollution control guideline for gaseous fuel is 0.5 pound $SO_2$ per $10^6$ Btu. It is equivalent to 520 ppm by volume of sulfur compounds per SCF of gas with a heating value of 175 Btu/SCF.

The overall efficiency required to meet EPA guidelines is $100 - 520 * 100/6190 = 91.6\%$.

The hydrogen sulfide removal efficiency of the commercial iron oxide boxes ranges from 85 to 95%. Assuming one dry box will give a 91.6% or more efficiency:

$C = 2$ (for one box)

It has been suggested in the literature that the oxide bed should be at least 10 ft thick for good gas distribution.

$D = 10$ ft.

$$A = \frac{(952{,}380)\ (515)}{(3000)\ (10+2)} = 13{,}630 \text{ ft}^2$$

Considering the limitation of physical size and the requirement of uniform gas distribution inside the iron oxide boxes, ten trains of gas clean-up units, in parallel, are suggested. The size of each box is

$13{,}630/10 = 1363$ ft$^2$

i.e., 41.7 ft I.D. × 10 ft high (cylindrical container)

37 ft × 37 ft × 10 ft high (rectangular container)

Total amount of $Fe_2O_3$ required is

1363 × 10 ft$^3$/box × 10 boxes × 9 lb $Fe_2O_3$/ft$^3$ = 1,226,700 lbs of $Fe_2O_3$.

Summary

Ten boxes of 37'×37'×10' (or 41.7' I.D. × 10') are required for treatment of 22.86 million cubic feet per day of producer gas with a heating value of 175 Btu per SCF.

B. Design Based on European Practices

1. For R = 20

952,380/20 = 47,600 ft$^3$ of oxide in box.

Assume the depth of bed height is 10 ft.

Cross-sectional area of box is 4760 ft$^2$.

Linear gas velocity = 952,380/4768/60 = 3.3 ft/min.

Mean gas residence time - 10/3.3 = 3.0 min.

Sulfur deposition rate is

952,380 × 3.68 × 0.92/60/4760 = 11.3 grain/ft$^2$/min

Sulfur deposition is below maximum rate of 15 grains/ft$^2$/min.

Considering the limitation of physical size and the requirement of uniform gas distribution inside the boxes, four boxes in parallel are suggested.

4760/4 - 1190 $ft^2$

i.e., 39 ft I.D. x 10 ft high

(4 columns are required)

Total amount of $Fe_2O_3$ required is 428,000 pounds.

2. For R = 50

952,380/50 = 19,050 $ft^3$ of oxide in box.

Cross-sectional area is

19,050/10 = 1905 $ft^2$

Linear gas velocity = 952,380/1905/60 = 8.3 ft/min.

Mean gas residence time = 10/8.3 - 1.2 min.

Sulfur deposition rate is

952,380 x 3.68 x 0.92/60/1905 = 27.6 grains/$ft^2$/min.

Since sulfur deposition rate is larger than acceptable value, 15, R equal to 50 cannot be used for design.

Table I lists designs at varying values of R.

## Summary

According to European design practices for iron oxide box, the values of R can be 20 or 25 for this case. The dimension of the boxes is:

39 ft I.D. x 10 ft high, 4 boxes required; for R = 20.

35 ft I.D. x 10 ft high, 4 boxes required; for R = 25.

## TABLE I: IRON OXIDE BOX DESIGN BASED ON EUROPEAN PRACTICES

| R CFH Gas per CF Oxide | Volume of Iron Oxide $Ft^3$ | Bed Depth Ft | Total Cross Sectional Area Needed $Ft^3$ | No.of Box Suggested | Linear Gas Velocity Ft/min | Mean Gas Residence Time, min | Rate of S Deposition Grains/$ft^2$ min | Box Dimension | No. of Boxes Required |
|---|---|---|---|---|---|---|---|---|---|
| 20 | 47,600 | 10 | 4,760 | 4 | 3.3 | 3.0 | 11.3 | 39' I.D. X 10' High | 4 |
| 25 | 38,100 | 10 | 3,810 | 4 | 4.1 | 2.4 | 14.1 | 35' I.D. x 10' High | 4 |
| 30 | 31,700 | 10 | 3,170 |  | 5.0 | 2.0 | 16.0 * |  |  |
| 50 | 19,050 | 10 | 1,905 |  | 8.3 | 1.2 | 27.6 * |  |  |

* Rate of sulfur deposition is greater than 15 grains/$ft^2$/min. limit.

## II. Liquid-phase Iron Oxide Process (Ferrox)

$H_2S$ must be removed from product gas to meet EPA guidelines:

$$3.68 \times 952{,}380 \times 0.92/7000 = 460.6 \text{ lbs } H_2S/\text{hr} = 0.128 \text{ lbs } H_2S/\text{sec}$$

$$2\ Fe\ (OH)_3 + 3\ H_2S \longrightarrow Fe_2S_3 + 6\ H_2O$$

$$\frac{3\ H_2S}{2\ Fe\ (OH)_3} = 1.5 \times \frac{(34)}{(58.5 + 51)} = 0.466\ \frac{\text{lb } H_2S}{\text{lb Fe } (OH)_3}\ \text{(theoretical)}$$

Theoretical amount of Fe $(OH)_3$ required to remove 0.128 lbs per sec of $H_2S$ is

$$0.128/0.466 = 0.275 \text{ lbs of Fe } (OH)_3/\text{sec} \qquad \text{(theoretical)}$$

Actual amount of Fe $(OH)_3$ used is usually about 3 times that of the theoretical one,

$$0.275 \times 3 = 0.825 \text{ lbs Fe } (OH)_3/\text{sec} \qquad \text{(actual use)}$$

This amount corresponds to 0.5 W % in scrubbing solution, the amount of solution is

$$0.825 \times \frac{100}{0.5} = 165 \text{ lbs solution/sec}$$

$$= 1161 \text{ gpm @ } 63.6 \text{ lb/ft}^3$$

$$\text{Scrubbing Solution}\left\{\begin{array}{l} 0.83 \text{ lb/sec : Fe } (OH)_3 \\ 4.94 \text{ lb/sec : } Na_2CO_3 \\ 158.93 \text{ lb/sec : } H_2O \end{array}\right\}\ \text{Total}\left\{\begin{array}{l} 165 \text{ lb/sec} \\ (2.59 \text{ ft}^3/\text{sec}) \end{array}\right.$$

Physical properties of gas and solution:

$\mu = 1.0$ cp

$\rho_g = 20/380 = 0.053$ lb/ft$^3$

$\rho_l = 63.6$ lb/ft$^3$

$\psi = \rho_{H2O}/\rho_l = 64.2/63.6 = 0.981$

$F_p$ = packing factor

= 40 for 2" Intalox Saddles

## Calculate Flooding Point for a Packed Column

$L' = 165$ lb/sec

$G' = 952{,}380 \times 0.053/3600 = 14.02$ lb/sec

The limiting vapor velocity for practical operation of a packed twoer is set by the flooding point. The flooding point can be predicted as presented in Perry's Chemical Engineer's Handbook or in the generalized pressure drop correlation of an aritcle by J. S. Eckert (Chemical Engineering Progress, Vol. 66, No. 3, March 1970, p. 40).

$$L/G\ (\rho_g/\rho_l)^{1/2} = \frac{L'}{G'}\ (\rho_g/\rho_l)^{1/2} = \frac{165}{14.02}\ \left(\frac{0.053}{63.6}\right)^{1/2} = 0.339$$

From the correlation, it is found that the value of ordinate is

$$\frac{G^2 F_p \Psi \mu^{0.2}}{\rho_g \rho_l\ g_c} = 0.063$$

$$G^2 = 0.063\ \frac{\rho_g \rho_l\ g_c}{F_p \Psi \mu^{0.2}}$$

$$G^2 = 0.063\ \frac{(0.053)\ (63.6)\ (32.2)}{(40)\ (0.981)\ (1.0)^{0.2}} = 0.174$$

$G = 0.418$ lb/ft$^2$ sec

Cross-sectional area of packed column at flooding point is

$14.02/0.418 = 33.6$ ft$^2$

The vapor velocity at flooding point is, $V_{gf}$,

$V_{gf} = 952{,}380/3600/33.6 = 7.9$ ft/sec

## Calculate Packed Tower Diameter

Because the packed column operation may become unstable as the flooding point is approached, the design value for allowable vapor velocity is usually estimated to be 50 to 70% of the maximum allowable velocity, and this allowable velocity is used to establish the column diameter. Say at 50%,

$V_g = V_{gf} \times 50\% = 7.9 \times 0.5 = 3.9$ ft/sec

$A = 952{,}380/3600/3.9 = 67.2$ ft$^2$

i.e., 9 ft 3 inch I.D. column.

Packed Bed Height

The height of packing material required can be estimated by

$$h = \frac{G_M}{K_G a P} N_{OG}$$

$$N_{OG} = \frac{\ln\left[\left(1 - \frac{mG_M}{L_M}\right)\left(\frac{y_1 - mx_2}{y_2 - mx_2}\right) + \frac{mG_M}{L_M}\right]}{1 - (mG_M/L_M)}$$

where $N_{OG}$ = number of overall transfer units

$m$ = slope of equilibrium curve $dy_e/dx$

$x_2$ = mole fraction solute in liquid fed to top of column

$y_1$ = mole fraction solute in gas fed to bottom of column

$y_2$ = mole fraction in gas leaving top of column

$G_M$ = superficial molar mass velocity of gas stream, lb moles/(hr)(sq ft)

$L_M$ = superficial molar mass velocity of liquid stream, lb moles/(hr)(sq ft)

The number of overall transfer units is estimated to be 15 from Perry's Handbook.

$$h = \frac{(14.02)\ (15)}{(20)\ (0.4)\ (1.0)} = 26.3 \text{ ft}$$

plus about 10 ft of freeboard for gas-liquid disengagement, 15 ft for bottom head, the overall height of the packed column is about 50 ft.

**Size of Regenerator**

It has been indicated in literature that a minimum 5 minutes of liquid mean residence time is required for regenerating ferric sulfide into ferric oxide.

$V = 2.59\ \text{ft}^3/\text{sec} \times 60 \times 5 = 777\ \text{ft}^3$

i.e., 7.0 ft I.D. x 20 ft high

**Summary**

**Packed Tower**

Packed column : 9 ft 3 inches I.D. x 50 ft overall height

Packing Height : 26 ft

Packing Material: 2" Intalox Saddles with $F_p = 40$

**Regenerator**

Total Volume Required: 777 $\text{ft}^3$

i.e., 7.0' I.D. x 20' High (for example)

**Flow Rates**

Product Gas: 952,380 SCFH or $22.86 \times 10^6$ SCFD

Solution Circulation Rate: 165 lb/sec or 1161 gpm

## III. Stretford Process

The amount of $H_2S$ to be removed from raw product gas to meet EPA guidelines is

$3.68\ \text{gr/SCF} \times 952{,}380\ \text{SCF/hr} \times 0.92/7000\ \text{gr/lb} =$

$460.6\ \text{lb}\ H_2S/\text{hr} = 0.128\ \text{lb}\ H_2S/\text{sec}.$

From process basic chemistry, it is shown that one mole of sodium carbonate is required to react with each mole of hydrogen sulfide.

i.e., $Na_2CO_3 + H_2S = NaHS + NaHCO_3$

$$\frac{Na_2CO_3}{H_2S} = \frac{106}{34} = 3.118 \quad \frac{\text{lb } Na_2CO_3}{\text{lb } H_2S}$$

Hence, theoretical amount of $Na_2CO_3$ required to absorb 0.128 pound per second of $H_2S$ is

$0.128 \times 3.118 = 0.399$ lb $Na_2CO_3$/sec.

Actual amount of $Na_2CO_3$ used in practical operation is usually about two to three times that of the theoretical one. Say three times,

$0.399 \times 3 = 1.197$ lbs $Na_2CO_3$/sec.

The scrubbing solution is an aqueous solution containing sodium carbonate and bicarbonate in the proportion of about 1:3 and 2,7 anthraquinone disulfonic acid (ADA). The concentration of $Na_2CO_3$ is about 0.1 N and $NaHCO_3$ is 0.3 N in order to keep the pH range of 8.5 to 9.5. This is equivalent to a solution with 0.505 W % of $Na_2CO_3$. Thus the amount of solution required is

$1.197 \times 100/0.505 = 237.1$ lb solution/sec

$= 1625$ gpm @ 65.5 lb/ft$^3$

The following physical properties of gas and solution have been estimated:

$\mu = 1.0$ cp

$\rho_g = 0.053$ lb/ft$^3$

$\rho_l = 65.5$ lb/ft$^3$

$\psi = \rho_{H_2O} / \rho_l = 0.952$

### Calculate Flooding Point of a Packed Column

$L' = 237.1$ lb/sec

$G' = 952{,}380 \times 0.053/3600 = 14.02$ lb/sec

$$\frac{L}{G}\left(\frac{\rho_g}{\rho_l}\right)^{1/2} = \frac{L'}{G'}\left(\frac{\rho_g}{\rho_l}\right)^{1/2} = \frac{237.1}{14.02}\left(\frac{0.053}{65.5}\right)^{1/2} = 0.48$$

From Perry's Chemical Engineers' Handbook, it is found that

$$\frac{G^2 F_p \psi \mu^{0.2}}{\rho_g \; \rho_l \, g_c} = 0.041$$

Assuming 2" saddles are used as a packing material with a packing factor of 40, i.e. $F_p = 40$

$$G = \left(0.41 \frac{\rho_g \rho_l g_c}{F_p \psi \mu^{0.2}}\right)^{1/2} = \left[\frac{(0.041)\ (0.053)\ (65.5)\ (32.2)}{(40)\ (0.952)\ (1.0)^{0.2}}\right]^{1/2}$$

$$= 0.347 \text{ lb/ft}^2 \text{ sec}$$

Cross-sectional area of packed column at flooding point is

$14.02/0.347 = 40.4$ ft$^2$

The vapor velocity at flooding point is

$952{,}380/3600/40.4 = 6.5$ ft/sec

### Calculate Packed Column Diameter

Assume the design value for allowable vapor velocity is 50% that of flooding point.

$V_g = 6.5 \times 0.5 = 3.3$ ft/sec

Thus, the cross-sectional area is

$A = 952{,}380/3600/3.3 = 80.2$ ft$^2$

i.e., 10 ft I.D.

## Packing Height

A mean residence time of 10 seconds is assumed.

$$3.3 \text{ ft/sec} \times 10 \text{ sec} = 33 \text{ ft.}$$

## Reaction Tank (Delay Tank)

The reaction tank is located at the bottom of the absorber tower. A minimum of 10 minutes holding time is required to ensure a complete sulfur deposition. The height of the reaction tank is

$$h = \frac{(2.371)\ (60)\ (10)}{(65.5)\ (80.2)} = 27 \text{ ft.}$$

## Oxidizer (Regenerator)

The oxidation of reduced ADA to normal ADA will take 20 to 60 minutes for completion. However, 10 to 15 minutes will be practically enough for recirculation of the solution. Say 15 minutes for this calculation. Then the size of the oxidizer is

$$\frac{237 \times 60 \times 15}{65.5} = 3260 \text{ ft}^3$$

i.e., 14 ft 6 inches I.D. x 20 ft high

(Twenty feet high is typical for oxidizer)

# APPENDIX C

## MATERIAL BALANCES ON NITROGEN AND SULFUR COMPONENTS FOR RILEY-MORGAN GASIFICATION SYSTEM

### 1. DATA

The following data are extracted from the paper presented by Rawdon et al.

A. Dry Gas Composition

| | V % |
|---|---|
| CO | 24.6 |
| $H_2$ | 13.1 |
| $CH_4$ | 4.4 |
| $CO_2$ | 5.9 |
| $N_2$ + A | 51.7 |
| $C_nH_m$ | 0.1 |
| $NH_3$ | 0.07 |
| $H_2S$ | 0.12 |

B. Average gas flow Rate is 40 scfm

C. Ammonia concentration in gas is 666 ppm

D. Carbon, nitrogen and sulfur contents of feed coal are 81.0 1.54 and 0.7 W %, respectively.

E. Molar conversion of coal nitrogen to ammonia is 9%

F. Tar loading in the gas is 0.8 grams/scf

G. Nitrogen and sulfur contents of tars in the gas are 1.2 and 0.5 W %, respectively.

### 2. CALCULATION

A. Back-calculation of coal feed rate

1) Based on nitrogen balance in gas

666 ppm $NH_3$ x 40 x 60 = 1.598 scfh of $NH_3$

1.598/380 x 17 = 0.0715 lbs of $NH_3$

= 0.0588 lbs of Nitrogen

0.0588 = 0.09 x 0.0154 x W

W = 42.4 lbs/hr of coal feed

2) Based on carbon balance and an assumed value of carbon conversion.

| Gas Component | Carbon Balance |
|---|---|
| CO | 24.6% x 40 x 60 = 590.4 scfh |
| $CH_4$ | 4.4% x 40 x 60 = 105.6 scfh |
| $CO_2$ | 5.9% x 40 x 60 = 141.6 scfh |
| $C_nH_m$ | 0.1% x 40 x 60 x 3 = 7.2 scfh |
| | 844.8 scfh |
| | 2.22 Moles/Hr |
| | 26.7 lbs/Hr |

If 80% of carbon in coal is in the gas, the the coal feed rate is 26.7/0.8/0.81 = 41.2 lbs/Hr.

Since both figures come out very close to each other, the coal feed rate is taken to be 42 lbs/Hr in subsequent calculations.

B. Sulfur-component balance

In: 42 x 0.7% = 0.294 lbs of sulfur per hour

Out: 0.12% x 40 x 60 x 32/380 = 0.243 lbs/Hr in $H_sS$

0.8 x 2400/453.6 x 0.5% = 0.021 lbs/Hr in Coal Tars

0.294 - 0.243 - 0.021 = 0.030 lbs/Hr in (Coke + Char)

C. Nitrogen-component balance

Accurate calculation of nitrogen balance is impossible because no data on the ratio of air feed rate to coal feed rate have been given. The nitrogen-component balance, however, is estimated as follows:

In: 42 x 1.54% = 0.647 lbs of N in Coal/Hr

Out: 0.07% x 40 x 60/380 x 14 = 0.062 lbs of N in $NH_3$

0.8 x 2400/543.6 x 1.2% = 0.051 lbs of N in Coal Tar

The balance 0.534 (0.647 - 0.062 - 0.051) appears as free nitrogen in the gas and as bonded nitrogen in the coke and char. According to data of Kohl, the split of the remaining nitrogen is estimated as 34% in coke and char and 66% in the gas.

Hence 0.534 x 34% = 0.182 lbs/Hr in Coke and Char

0.534 x 66% = 0.352 lbs/Hr in Gas as $N_2$

## 3. SUMMARY

### A. Sulfur Balance

| In, lb/Hr | Out, lb/Hr | | |
|---|---|---|---|
| Coal | $H_2S$ | Tars | Coke & Char |
| 0.294 | 0.253 | 0.021 | 0.030 |
| (100%) | (82.65%) | (7.14%) | (10.21%) |

### B. Nitrogen Balance

| In, lb/Hr | Out, lb/Hr | | | |
|---|---|---|---|---|
| Coal | $NH_3$ | Tars | $N_2$ | Coke + Char |
| 0.647 | 0.062 | 0.051 | 0.352 | 0.182 |
| (100%) | (9.58%) | (7.88%) | (54.50%) | (28.14%) |